Supporting Information for:

Dynamic Diastereoselectivity During Iron Carbonyl Mediated Spirocyclization Reactions

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Experimental Section

General Methods: All glassware used was oven dried (overnight at 140 °C) or flame dried prior to use. Organic solvents/reagents were purified prior to use as follows: THF, diethyl ether, benzene and toluene were freshly distilled from Na/benzophenone; CH_3CN and CH_2Cl_2 were distilled from CaH_2; n-Bu_2O was distilled from Na; All other solvents were used as purchased. Column chromatography was performed with silica gel (0.04-0.063 mm). Eluting solvents are reported as V/V percent mixture. All yields given refer to as isolated yields. Optical rotations were measured on a precision automated polarimeter. NMR spectra were recorded on a 200 MHz or 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane. HRMS experiments were performed on a high resolution magnetic sector mass spectrometer. Melting points are uncorrected.

(4*S*, 2*E*)-Ethyl 4-[tert-butoxycarbonyl-(4-methoxybenzyl)amino]-5-phenylpent-2-enoate (6). To a solution of ethyl 2-(diethoxyphosphoryl)propanoate (0.51 g, 2.26 mmol) in THF (23 mL) under Ar at -78 °C, was slowly added *n*-BuLi (0.83 mL, 2.5 M in hexanes, 2.07 mmol) via a syringe. The reaction mixture was stirred at this temperature for 1 h. A solution of aldehyde **5** (0.70 g, 1.89 mmol) in THF (5.5 mL) was added, then the mixture was stirred at -78 °C for 3 h. After the temperature was allowed to rise to rt over 30 min, the reaction mixture was quenched with sat. aq. NH_4Cl (10 mL) and extracted with Et_2O (12 mL x 3). The combined organic layer was washed with brine (10 mL), dried (Na_2SO_4), filtered and concentrated in vacuo. The crude product was purified by flash chromatography (Hex:EA/8:1) to provide **6** (0.44 g, 53%). R_f = 0.70 (Hex:EA/4:1). $[\alpha]_D^{25}$ = -53 (*c* = 1.26, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22-6.90 (7H), 6.74 (d, *J* = 8.4 Hz, 2H), 6.50-6.30 (br, 1H), 5.66 (d, *J* = 11.2 Hz, 1H), 5.50-5.20 (br, 1H), 4.40-4.15 (br, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.77 (s, 3H), 3.40-3.00 (br, 1H), 2.96-2.82 (m, 1H), 1.47 (s, 9H), 1.25 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.0, 158.8, 147.8, 138.2, 130.9, 129.6, 129.1, 128.5, 126.4, 119.4, 113.8, 60.3, 59.4, 57.5, 55.4, 52.5, 38.2, 28.8, 14.4. HRMS (FAB) calcd for MH^+ ($C_{26}H_{34}NO_5$) 440.2437, found, 440.2435. This

reaction also afforded (4*S*, 2*Z*)-ethyl 4-[tert-butoxycarbonyl-(4-methoxybenzyl)amino]-5-phenylpent-2-enoate in 39% yield. R_f = 0.75 (Hex:EA/4:1). $[\alpha]_D^{25}$ = +97 (*c* = 2.74, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.06 (7H), 7.00-6.82 (br, 1H), 6.78 (d, *J* = 8.8 Hz, 2H), 5.80-5.60 (br, 1H), 4.65-4.20 (m, 2H), 4.15 (q, *J* = 6.8 Hz, 2H), 4.00-3.80 (br, 1H), 3.78 (s, 3H), 3.20-3.00 (br, 1H), 2.91 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.44 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 138.0, 129.4, 128.7, 126.8, 114.0, 60.6, 59.5, 55.5, 49.9, 28.6, 14.4. Some peaks were not recorded due to the presence of amide resonance rotamers. HRMS (FAB) calcd for MH^+ ($C_{26}H_{34}NO_5$) 440.2437, found, 440.2430.

(4*S*, 2*E*)-Ethyl 4-(4-methoxy-benzylamino)- 5-phenylpent-2-enoate (7). Ester **6** (322 mg, 0.73 mmol) was dissolved in dry CH_2Cl_2 (3.8 mL) and cooled to 0 °C. TFA (1.9 mL) was added slowly to the reaction solution, which was then stirred at the same temperature for 1h, quenched by aq sat $NaHCO_3$ solution at 0 °C (pH = 8-9), and extracted with CH_2Cl_2 (5mL x 3). The combined organic layer was dried (Na_2SO_4), filtered and concentrated in vacuo. The crude product **7** (236 mg, 96%) was used in the next reaction without further purification. $[\alpha]_D^{25}$ = -27 (*c* = 1.18, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.04 (7H), 6.85 (dd, *J* = 15.6, 7.6 Hz, 1H), 6.80 (dt, *J* = 8.4, 1.6 Hz, 2H), 5.92 (dd, *J* = 15.6, 0.8 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.78 (s, 3H), 3.73, 3.51 (ABq, *J* = 13.2 Hz, 2H), 3.48-3.44 (m, 1H), 2.85 (dd, *J* = 14.4, 6.0 Hz, 1H), 2.76 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.43 (br, 1H), 1.30 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 158.8, 150.4, 137.8, 132.2, 129.5, 129.3, 128.8, 126.9, 122.3, 114.0, 60.6, 59.9, 55.5, 51.0, 41.9, 14.5. HRMS (FAB) calcd for MH^+ ($C_{21}H_{26}NO_3$) 340.1913, found, 340.1918.

(4*S*, 2*E*)-Ethyl 4-[tert-butoxycarbonyl-(4-methoxybenzyl)amino]-2-methyl-5-phenyl-pent-2-enoate (13) and (4*S*, 2*Z*)-ethyl 4-[tert-butoxycarbonyl-(4-methoxybenzyl)amino]-2-methyl-5-phenyl-pent-2-enoate (14). Method A: To a solution of ethyl 2-(diethoxyphosphoryl) propanoate (3.50 g, 14.6 mmol) in THF (82 mL) under Ar at -78 °C, was slowly added *n*-BuLi (5.2 mL, 2.5 M in hexanes, 13.0 mmol) via a syringe. The reaction mixture was stirred at this temperature for 30 min and

then warmed to 0 °C for 10 minutes. The temperature was again cooled to -78 °C, aldehyde **5** (2.99 g, 8.1 mmol) dissolved in THF (20 mL) was added, and the mixture was stirred at -78 °C for 3 h. After the temperature was allowed to rise to rt for 15 min, the reaction mixture was quenched with sat. aq NH_4Cl (30 mL) and extracted with Et_2O (40 mL x 3). The combined organic layer was washed with brine (20 mL), dried (Na_2SO_4), filtered and concentrated in vacuo. The product was purified by flash chromatography (Hex:EA/6:1) to provide **13** (2.40 g, 67%, ee = 94%, $[\alpha]_D^{25}$ = -2.9 (*c* = 5.07, $CHCl_3$)) and **14** (0.50 g, 14%, $[\alpha]_D^{25}$ = +73 (*c* = 0.80, $CHCl_3$)) as colorless viscous oils. **Method B**: To a solution of ethyl 2-(diethoxyphosphoryl)propanoate (199 mg, 0.83 mmol) in CH_3CN (5.5 mL), was added LiCl (36.0 mg, 0.83 mmol, dried in a vacuum oven), followed by DBU (0.13 mL, 0.83 mmol). The reaction mixture was stirred at rt for 20 min until the LiCl dissolved completely, then cooled to 0 °C. Aldehyde **5** (190 mg, 0.51 mmol) in CH_3CN (0.5 mL) was added dropwise via syringe and the reaction mixture was stirred at 0 °C for 3 h (monitored by TLC). The same workup and purification procedure as method A afforded **13** (150 mg, 65%, ee = 74%) and **14** (30mg, 13%) as colorless viscous oils. **Method C**: To a solution of aldehyde **5** (115 mg, 0.31 mmol) in CH_2Cl_2 (0.5 mL), was added a solution of (carbethoxyethylidene)triphenylphosphorane (141 mg, 0.39 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C. Then the temperature was allowed to rise to rt and the mixture was stirred for 22 h. The same workup and purification procedure as method A afforded **13** (103 mg, 73%, ee = 71%) and **14** (18 mg, 13%). **13**: R_f = 0.50 (Hex:EA/4:1). ^{1}H NMR (200 MHz, DMSO-d): δ 7.35-7.05 (7H), 6.86-6.82 (d, *J* = 8.2 Hz, 2H), 6.76-6.72 (d, *J* = 8.0 Hz, 1H), 4.90-4.62 (s, br, 1H), 4.30 (s, 3H), 4.05 (q, *J* = 7.0 Hz, 2H), 3.72 (s, 3H), 3.09-2.78 (2H), 1.49 (s, 3H), 1.35 (s, 9H), 1.16 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 167.8, 158.7, 155.6, 139.0, 137.9, 131.1, 129.3, 128.8, 128.4, 126.5, 113.8, 80.2, 60.7, 56.2, 55.3, 48.7, 39.8, 39.7, 28.5, 14.3, 12.5. HRMS (FAB) calcd for MH^+ ($C_{27}H_{36}NO_5$) 454.2593, found, 454.2593. **14**: R_f = 0.65 (Hex:EA/4:1).. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.21-6.70 (9H), 6.50-6.00 (br, 1H), 5.20-5.00 (br, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 4.30-4.00 (br, 1H), 3.78 (s, 3H), 3.40-3.00 (br, 1H), 2.80-2.75 (m, 1H), 1.83 (s, 3H), 1.46 (s, 9H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (50 MHz,

$CDCl_3$): δ 167.2, 158.5, 140.3, 138.8, 130.9, 129.4, 128.8, 128.2, 127.9, 127.8, 126.2, 113.6, 60.4, 55.3, 29.6, 20.6, 14.3. HRMS (FAB) calcd for MH^+ ($C_{27}H_{36}NO_5$) 454.2593, found, 454.2586.

(5*S*)-5-Benzyl-1-(4-methoxybenzyl)-3-methyl-1,5-dihydropyrrol-2-one (15). Compound **14** (90 mg) was dissolved in dry CH_2Cl_2 (1 mL) and cooled to 0 °C. TFA (0.5 mL) was then added slowly to the reaction mixture, which was stirred at the same temperature for 15 min, quenched by slow addition of sat $NaHCO_3$ solution (10 mL) at 0 °C, extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated to give **15** (61 mg, 100%) as a light yellow oil. R_f = 0.47 (Hex:EA/19:1). ^{1}H NMR (200 MHz, $CDCl_3$): 7.40-6.80 (9H), 6.48 (t, *J* = 1.6 Hz, 1H), 5.14 (d, *J* = 15.0 Hz, 1H), 4.11 (d, *J* = 15.0 Hz, 1H), 4.00-3.85 (m, 1H), 3.78 (s, 3H), 3.15 (dd, *J* = 13.2, 5.6 Hz, 1H), 3.48 (dd, *J* = 13.2, 9.3 Hz, 1H), 1.88 (t, *J* = 1.7 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): 171.9, 159.0, 140.2, 136.7, 134.9, 129.8, 129.3, 129.2, 128.6, 126.9, 114.1, 60.5, 55.3, 43.7, 38.0, 11.3. HRMS (FAB) calcd for MH^+ ($C_{20}H_{22}NO_2$) 308.1650, found, 308.1646.

(4*S*, 2*Z*)-Ethyl 4-(4-methoxybenzylamino)-2-methyl-5-phenylpent-2-enoate (16). Following the procedure for preparation of compound **7**, compound **13** (600 mg, 1.32 mmol) was dissolved in dry CH_2Cl_2 (6 mL) and cooled to 0 °C, followed by addition of TFA (3 mL). Stirring was continued for 1h. Crude product **16** was used in the following reaction without further purification. R_f = 0.50 (Hex:EA/1:1). $[\alpha]_D^{25}$ = +3.4 (*c* = 1.02, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.16 (2H), 7.11 (dt, *J* = 6.8, 1.6 Hz, 2H), 7.04 (dt, *J* = 8.4, 2.0 Hz, 2H), 6.78 (dt, *J* = 8.8, 2.0 Hz, 1H), 6.62-6.59 (m, 1H), 4.17 (dq, *J* = 14.4, 0.4 Hz, 2H), 3.76 (s, 3H), 3.66-3.62 (m, 1H), 3.73 and 3.49 (ABq, *J* = 13.2 Hz, 2H), 2.81-2.68 (2H), 1.60 (d, *J* = 1.2 Hz, 3H), 1.46 (s, *br*, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 168.1, 158.8, 144.2, 138.0, 132.4, 129.6, 129.3, 128.6, 126.7, 113.9, 60.8, 56.8, 55.4, 51.2, 41.7, 14.4, 12.9. HRMS (FAB) calcd for MH^+ ($C_{22}H_{28}NO_3$) 354.2069, found, 354.2075.

Preparation of racemic N-(tert-butoxycarbonyl)-N-(methoxybenzyl)-L-phenylalaninal (5). To a solution of aldehyde **5** (88 mg, 0.24 mmol) in freshly distilled acetonitrile (25 mL) at 0 °C, was added lithium chloride (17 mg, 0.4mmol, dried in a vacuum oven) and DBU (0.06 mL). The reaction mixture

was stirred at this temperature for 2 h, quenched by 1 N HCl (5 mL), and extracted with ether (15 mL x 3). The combined organic phase was dried (Na_2SO_4), filtered and concentrated in vacuo. Purification by flash chromatography (Hex:EA/ 2:1) afforded racemic aldehyde **5** (75 mg, 85%) as a colorless oil.

(4*S*, 2*E*)-Ethyl 4-(N-(4-methoxybenzyl)-((2*S*)-3,3,3-trifluoro-2-ethoxy-2-phenylpropanoxamido))-2-methyl-5-phenylpent-2-enoate (17a) and (4*R*, 2*E*)-ethyl 4-(N-(4-methoxybenzyl)-((2*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoxamido))-2-methyl-5-phenylpent-2-enoate (17b). To a solution of racemic amine **16** (4.0 mg, 11.4 μmol) and diisopropylethylamine (9.3 μL, 56.8 μmol) in freshly distilled CH_2Cl_2 (0.30 mL), was added Mosher's chloride (8.6 μL, 56.8 μmol) under argon. The reaction solution was stirred at rt for 12 h, quenched with 1 N HCl (0.5 mL), and extracted with CH_2Cl_2 (1 mL x 3). The combined organic layer was washed with brine (1 mL), dried (Na_2SO_4), filtered and concentrated in vacuo. Purification by preparative TLC (Hex:EA/ 6:1) afforded **17a** (2.5 mg, 41%) as a colorless oil. R_f = 0.35 (Hex:EA/4:1). Two rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) Major rotamer: δ 7.61-6.42 (15H), 4.44-4.38 (m, 1H), 4.37 and 4.00 (ABq, *J* = 14.8 Hz, 2H), 4.26-4.15 (2H), 3.74 (s, 3H), 3.53 (q, *J* = 2.0 Hz, 3H), 3.35 (dd, *J* = 7.6, 13.6 Hz, 1H), 2.79 (dd, *J* = 8.8, 13.6 Hz, 1H), 1.33 (t, *J* = 5.4 Hz, 3H), 1.29 (d, *J* = 1.2 Hz, 3H). Minor rotamer: δ 7.61-6.35 (15H), 5.00, 4.59 (ABq, *J* = 14.8 Hz, 2H), 4.06-4.01 (2H), 3.82 (s, 3H), 3.66 (q, *J* = 2.0 Hz, 3H), 3.06 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.72 (dd, *J* = 13.6, 8.8 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.21 (d, *J* = 1.6 Hz, 3H). HRMS (FAB) calcd for MH^+ ($C_{32}H_{35}F_3NO_5$) 570.2467, found, 570.2475. **17b** (2.7 mg, 42%, colorless oil). R_f = 0.30 (Hex:EA/4:1). Two rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) Major rotamer: δ 7.70-6.00 (15H), 4.93-4.80 (m, 1H), 4.85 and 4.66 (ABq, *J* = 15.2 Hz, 2H), 4.18-4.09 (2H), 3.81 (s, 3H), 3.40 (q, *J* = 1.6 Hz, 3H), 2.56 (dd, *J* = 12, 12 Hz, 1H), 2.26 (dd, *J* = 3.2, 13.4 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 1.6 Hz, 3H). Minor rotamer: δ 7.65-6.40 (15H), 4.60, 4.02 (ABq, *J* = 15.2 Hz, 2H), 4.44-4.38 (m, 1H), 3.76 (s, 3H), 3.60 (q, *J* = 1.6 Hz, 3H), 3.25 (dd, *J* = 13.6, 9.2 Hz, 1H), 3.00 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.42 (d, *J* = 1.6 Hz, 3H). HRMS (FAB) calcd for MH^+ ($C_{32}H_{35}F_3NO_5$) 570.2467, found, 570.2460.

Preparation of tricyclic lactam 22a and 22b via a Diels-Alder reaction. Method A: To a small vial was added the mixture of **18a** and **18b** (10.0 mg, 16.7 μmol) and sat. $CuCl_2$ solution in EtOH (0.3 mL). The reaction solution was stirred at rt for 24 h and then concentrated in vacuo. Water (1.5 mL) was added to the residue, which was extracted with ether (2 mL x 3). The combined ether layers were washed with brine (1.5 mL), dried (Na_2SO_4), filtered and concentrated in vacuo. Purification by preparative TLC (Hex:EA/3:1) afforded inseparable **22a** and **22b** (6.5 mg, 86%) in 9:1 ratio as a colorless oil. **Method B**: To a solution of methanesulfonyl chloride (42 μL, 0.54 mmol) in freshly distilled CH_2Cl_2 (2.0 mL) under argon at 0 °C, was slowly added a solution of carboxylic acid **26** (45 mg, 0.36 mmol) and diisopropylethylamine (78 μL, 0.47 mmol) in freshly distilled CH_2Cl_2 (1.3 mL). Stirring was continued at this temperature for 1 h, then diisopropylethylamine (0.13 mL, 0.80 mmol) was added, followed by a solution of amine **16** (204 mg, 0.58 mmol) in freshly distilled CH_2Cl_2 (1.6 mL). The temperature was allowed to reach rt and the reaction mixture was stirred for 20 h, and quenched with 1 N HCl (3 mL). After addition of CH_2Cl_2 (10 mL), the organic layer was washed with 1 N HCl (3 mL x 2) and brine (5 mL), dried (Na_2SO_4), filtered and concentrated in vacuo. The crude product was purified by flash chromatography (Hex:EA/8:1) to provide **22a** and **22b** (140 mg, 84%) in 9:1 ratio.

Preparation of Compound 23 from reduction of tricyclic lactam 22a and 22b. Following the procedure to prepare **12a** and **12b**, the mixture of **22a** and **22b** (11.0 mg, 24.0 μmol) was hydrogenated in MeOH (1 mL) in the presence of 10% Pd/C (5 mg). Removal of solvent in vacuo provided **23** (10.8 mg, 98%) as a colorless solid without further purification. R_f = 0.30 (4% MeOH in CH_2Cl_2). MP 110-114 °C. $[\alpha]_D^{25}$ = –28 (*c* = 0.95, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-6.68 (9H), 4.99 and 3.82 (ABq, *J* = 15.2 Hz, 2H), 4.14-4.05 (2H), 3.78 (s, 3H), 3.65-3.60 (m, 1H), 3.06-2.93 (2H), 2.80 (dd, *J* = 9.6, 1.6 Hz, 1H), 1.86-1.74 (3H), 1.64-1.40 (5H), 1.20 (t, *J* = 6.8 Hz, 3H), 0.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.5, 177.5, 158.9, 138.9, 129.4, 129.3, 129.2, 128.6, 126.6, 113.9, 61.2, 57.3, 55.5,

46.3, 45.8, 43.4, 41.8, 40.0, 35.1, 26.3, 23.7, 23.1, 20.8, 19.1, 14.3. HRMS (FAB) calcd for MH^+ ($C_{29}H_{36}NO_4$) 462.2644, found, 462.2644.

(2*S*)-Methyl 2-(4-methoxybenzylamino)-3-phenylpropanoate (31). To a solution of (*S*)-methyl 2-amino-3-phenylpropanoate hydrochloride (**30**) (1.0 g, 4.6 mmol) in MeOH (26 mL) which was neutralized with NaOH (0.19 g, 4.8 mmol), anisaldehyde (0.94 g, 6.8 mL) and acetic acid (0.26 mL, 4.6 mmol) were added at room temperature. After stirring for 10 min at this temperature, the solution was cooled with an ice bath and $NaBH_4$ pellets (0.17 g, 4.6 mmol) were added. The reaction mixture was stirred for 1 h at 0 °C, then the solvent was evaporated in vacuo. The residue was dissolved in ethyl acetate (25 mL) and the solution was filtered, then washed with saturated sodium carbonate solution (15 mL x 2) and dried (Na_2SO_4). Further purification by flash chromatography (Hex:EA/3:1) afforded **31** (1.13 g, 82%, ee = 100%) as a colorless oil. R_f = 0.45 (Hex:EA/2:1). $[\alpha]_D^{25}$ = –5 (*c* = 0.63, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-6.78 (9H), 3.78 (s, 3H), 3.74 and 3.57 (ABq, *J* = 12.8 Hz, 2H), 3.53 (dd, *J* = 7.2, 7.2 Hz, 1H), 2.96-2.94 (2H), 1.78 (s, br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.3, 158.9, 137.6, 131.9, 129.6, 129.4, 128.6, 126.9, 114.0, 62.2, 55.5, 51.9, 51.6, 40.0. HRMS (FAB) calcd for MH^+ ($C_{18}H_{22}NO_3$) 300.1600, found, 300.1602.

(2*S*)-Methyl 2-[N-(4-methoxybenzyl)-((2*S*)- 3, 3, 3-trifluoro-2-methoxy-2-phenyl propanoxamido))]-3-phenylpropanoate (32). Following the procedure to prepare **17a** and **17b**, compound **31** (9.5 mg, 0.032 mmol) was dissolved in CH_2Cl_2 (0.4 mL), and diisopropylethylamine (32 μL, 0.191 mmol) was added. To this mixture, was added (2*S*)-3, 3, 3-trifluoro-2-methoxy-2-phenyl propionyl chloride (Mosher's chloride, 24μL, 0.128 mmol), and stirring was continued for 14 h at rt. The solvent was evaporated, and the residue was held under vacuum oil pump for 12 h to afford **32** (15.0 mg, 91%). This material was not further purified to avoid fractionation of the diastereomers and erroneous determination of de. R_f = 0.50 (Hex:EA/2:1). Two rotamers. ^{1}H NMR (400 MHz, $CDCl_3$) Major rotamer: δ 7.64-6.42 (15H), 4.30 and 4.24 (ABq, *J* = 16.0 Hz, 2H), 3.97 (dd, *J* = 6.8, 6.40 Hz, 1H), 3.83 (q, *J* = 2.0 Hz, 3H), 3.76 (s, 3H), 3.70 (s, 3H), 3.65 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.91 (dd, *J* =

14.0, 6.4 Hz, 1H). ^{19}F NMR (400 MHz, $CDCl_3$) Major rotamer: δ 66.51. ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 167.1, 159.7, 138.5, 134.2, 130.7, 129.7, 129.6, 128.7, 128.4, 127.1, 126.7, 126.6, 114.2, 76.9, 60.9, 56.3, 55.5, 52.4, 51.8, 35.7. HRMS (FAB) calcd for MH^+ ($C_{28}H_{29}F_3NO_5$) 516.1998, found, 516.1960.

(2*S*)-Ethyl 2-[(3*S*, 4*S*)-3-benzyl-2-(4-methoxybenzyl)-1-oxo-2-azaspiro[4.5]decadien-4-yl]propanoate (36). The procedure was the same as for the preparation of compound **12a** and **12b**. The mixture of decomplexed products **29a** and **29b** (6.2 mg, 13.5 μmol) in methanol (0.7 mL) was hydrogenated over 10% Pd/C (6 mg) for 24 h. The crude product was purified by preparative TLC (Hex:EA/2:1) to afford **36** (5.2 mg, 84%) as a colorless oil. R_f = 0.50 (Hex:EA/2:1). $[\alpha]_D^{25}$ = +21 (*c* = 0.49, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30- 6.83 (9H), 4.67 and 4.27 (ABq, *J* = 14.8 Hz, 2H), 3.98-3.86 (2H), 3.79 (s, 3H), 3.61 (ddd, *J* = 12.0, 4.4, 2.0 Hz, 1H), 2.89 (dd, *J* = 13.2, 4.0 Hz, 1H), 2.58 (dq, *J* = 7.2, 2.7 Hz, 1H), 2.46 (dd, *J* = 13.4, 10.4 Hz, 1H), 2.02 (dd, *J* = 2.4, 2.0 Hz, 1H), 1.87-1.21 (10H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.46 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 179.3, 174.8, 159.1, 138.1, 130.3, 129.9, 129.8, 128.8, 126.9, 114.1, 61.1, 60.7, 55.5, 46.9, 46.6, 46.0, 41.4, 38.0, 37.6, 28.8, 25.7, 23.0, 22.6, 16.3, 14.2. HRMS (FAB) calcd for MH^+ ($C_{29}H_{38}NO_4$) 464.2800, found, 464.2807.

(2*S*)-2-[(3*S*, 4*S*)-3-Benzyl-2-(4-methoxybenzyl)-1-oxo-2-azaspiro[4.5]decadien-4-yl]propyl (2*S*)-3, 3, 3-trifluoro-2-methoxy-2-phenylpropanoate (37). Following the procedure forthe preparation of **25**, a solution of ester **36** (3.0 mg, 6.4 μmol) in freshly distilled ether (0.2 mL) was treated with $LiBH_4$ (1.28 mg, 58.3 μmol) at rt for 2 h. The crude product, (2*S*)-2-[(3*S*, 4*S*)-3-benzyl-2-(4-methoxybenzyl)-1-oxo-2-azaspiro[4.5]decadien-4-yl]propanol, was used in the following reaction without any further purification. R_f = 0.20 (Hex:EA/1:1). $[\alpha]_D^{25}$ = -12 (*c* = 0.20, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31- 6.87 (9H), 4.96 and 3.94 (ABq, *J* = 14.4 Hz, 2H), 3.81 (s, 3H), 3.23-3.18 (3H), 2.56 (dd, *J* = 12.8, 10.0 Hz, 2H), 1.98 (s, br, 1H), 1.84-0.74 (12 H), 0.23 (d, *J* = 6.8 Hz, 3H). To a solution of the crude product (2.0 mg, 4.7 μmol) in freshly distilled benzene (0.15 mL), was added

diisopropylethylamine (11.2 μL, 66.4 μmol) and Mosher's chloride (10.8 μL, 57.0 μmol). The reaction mixture was heated to 80 °C and stirred for 24 h at this temperature. The cooled reaction mixture was quenched with 1 N HCl (0.6 mL) and extracted with ether (1 mL x 3). The combined organic layer was washed with brine (1 mL), dried (Na_2SO_4), filtered and concentrated in vacuo. The crude product **37** (2.8 mg, de > 86%, 70% yield over two steps) was subjected to ^{1}H NMR without any further purification for determination of de. R_f = 0.70 (Hex:EA/3:2). $[\alpha]_D^{25}$ = -3 (*c* = 0.23, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) Major isomer: δ 7.37- 6.83 (9H), 4.99 and 3.97 (ABq, *J* = 14.4 Hz, 2H), 3.92 (d, *J* = 2.8 Hz, 1H), 3.78 (s, 3H), 3.44 (q, *J* = 0.8 Hz, 3H), 3.23-3.13 (3H), 2.54 (dd, *J* = 12.0, 2.0 Hz, 1H), 2.00 (s, br, 1H), 1.90-1.20 (11H), 0.10 (d, *J* = 6.8 Hz, 3H). ^{19}F NMR (400 MHz, $CDCl_3$) Major isomer: δ –72.0, 93%; Minor isomer : δ –72.1, 7%. ^{13}C NMR (100 MHz, $CDCl_3$) Major isomer: δ 178.7, 166.2, 159.5, 137.8, 132.4, 130.5, 129.8, 128.9, 128.6, 128.4, 127.5, 127.1, 114.5, 77.4, 68.4, 57.9, 55.4, 46.8, 44.4, 40.2, 37.4, 31.8, 28.6, 25.6, 23.2, 22.6, 15.9. HRMS (FAB) calcd for MH^+ ($C_{37}H_{43}F_3NO_5$) 638.3093, found, 638.3056.

Preparation of tricyclic lactam 39 through a Diels-Alder reaction. Following the procedure for the preparation of compounds **22a** and **22b**, the mixture of *Z*-substrates **35a** and **35b** (11.5 mg, 19.2 μmol) was treated with saturated ethanolic $CuCl_2$ (0.35 mL) for 24 h to give compound **39** (7.0 mg, 81%) as a colorless oil which was purified by preparative TLC (Hex:EA/3:1). R_f = 0.35 (Hex:EA/2:1). $[\alpha]_D^{25}$ = +25 (*c* = 0.65, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27- 6.65 (9H), 4.99 and 3.86 (ABq, *J* = 14.8 Hz, 2H), 4.16-3.99 (2H), 3.94-3.89 (m, 1H), 3.76 (s, 3H), 3.48 (d, *J* = 15.2 Hz, 1H), 2.82-2.75 (2H), 1.8-1.2 (5H), 1.37 (s, 3H), 1.18 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 175.5, 158.8, 138.5, 137.9, 130.4, 129.6, 129.1, 129.0, 128.7, 126.6, 113.8, 60.8, 59.3, 55.5, 55.4, 51.2, 48.3, 43.7, 40.4, 39.3, 28.9, 27.7, 18.4, 14.3. HRMS (FAB) calcd for MH^+ ($C_{29}H_{34}NO_4$) 460.2488, found, 460.2489.

(2*S*, 3*Z*)-tert-Butyl 5-hydroxy-2-(N-4-methoxybenzyl)-4-methyl-1-phenylpent-3-en-2-yl carbamate (44). To a solution of **14** (133 mg, 0.294 mmol) in CH_2Cl_2 (4.0 mL) at -78 °C, was added

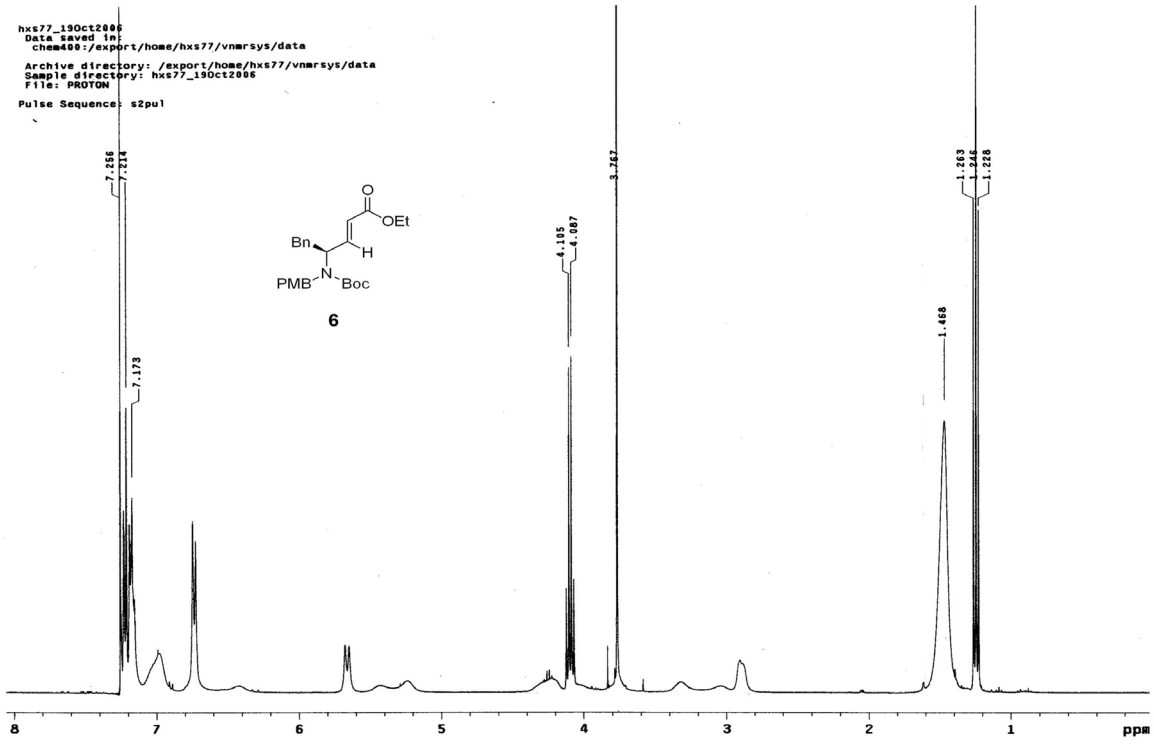
dropwise DIBAl-H solution (1.5 M in toluene, 0.78 mL, 1.174 mmol). Stirring was continued at -78 °C for 1 h, and then the reaction was quenched slowly with MeOH (1.5 mL) at this temperature, followed by addition of water (2.0 mL). After the reaction mixture was allowed to reach rt, it was extracted with CH_2Cl_2 (4 mL x 3) and the organic layer was dried (Na_2SO_4). The solvent was evaporated in vacuo, and the residue was purified by flash chromatography (Hex:EA/2:1) to provide **44** (110 mg, 92%) as a colorless oil. R_f = 0.15 (Hex:EA/4:1). $[\alpha]_D^{25}$ = -3 (*c* = 0.87, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.27-6.82 (9H), 5.34 (d, *J* = 10.1 Hz, 1H), 5.10-4.8- (br, 1H), 4.33 (s, 2H), 3.80 (s, 3H), 3.90-3.70 (m, 1H), 3.70-3.50 (m, 1H), 2.92 (dd, *J* = 13.2, 5.9 Hz, 1H), 2.73 (dd, *J* = 13.0, 8.8 Hz, 1H), 1.66 (d, *J* = 1.2 Hz, 3H), 1.41 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 158.6, 155.8, 138.5, 131.8, 129.4, 128.5, 128.3, 126.4, 125.6, 113.7, 113.6, 80.3, 61.5, 55.3, 47.5, 40.6, 40.5, 29.5, 21.8. HRMS (FAB) calcd for MH^+ ($C_{25}H_{34}NO_4$) 412.2488, found, 412.2483.

(2*S*, 3*Z*)-tert-Butyl 4-formyl-2-(N-4-methoxybenzyl)-1-phenylpent-3-en-2-ylcarbamate (45). To a solution of alcohol **44** (95 mg, 0.231 mmol) in benzene (1.7 mL), was added $Fe(CO)_4PPh_3$ (30 mg, 0.069 mmol) and trimethylamine oxide (52 mg, 0.693 mmol). After stirring for 12 h, the reaction mixture was filtered through Celite, then $Fe(CO)_4PPh_3$ (30 mg, 0.069 mmol) and trimethylamine oxide (52 mg, 0.693 mmol) was added to the filtrate. The mixture was maintained at rt for a further 12 h. After a second filtration, the solvent was evaporated in vacuo. The residue was purified by flash chromatography (Hex:EA/8:1) to afford aldehyde **45** (67 mg, 71%) as a colorless oil. R_f = 0.70 (Hex:EA/4:1). $[\alpha]_D^{25}$ = +47 (*c* = 0.62, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 9.61 (s, 1H), 7.26-6.80 (9H), 6.55 (br, 1H), 5.35-5.20 (m, 1H), 4.30 (br, 2H), 3.80 (s, 3H), 3.20-2.80 (2H), 1.63 (d, *J* = 1.2 Hz, 3H), 1.46 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 190.6, 158.9, 144.5, 137.4, 136.8, 130.7, 129.3, 128.8, 128.6, 128.4, 126.8, 114.0, 80.6, 55.4, 54.2, 40.3, 40.2, 29.5, 16.4. HRMS (FAB) calcd for MH^+ ($C_{25}H_{32}NO_4$) 410.2331, found, 410.2336.

(2*S*, 3*Z*)-tert-Butyl 2-(N-4-methoxybenzyl)-4-methyl-1-phenylhexa-3, 5-dien-2-ylcarbamate (46). To a suspension of methyltriphenylphosphonium bromide (91 mg, 0.254 mmol) in THF (2.0 mL) at 0

°C, was slowly added n-BuLi (2.5 M solution in hexanes, 86 μL, 0.215 mmol). After 45 min at this temperature, the mixture was cooled to -78 °C and then a solution of aldehyde **45** (80 mg, 0.196 mmol) in THF (1.0 mL) was added quickly. Stirring was continued at -78 °C for 30 min, then the reaction was allowed to warm to rt and maintained at this temperature for 2 h. Finally, the reaction was quenched with 1 N HCl (3 mL) and extracted with Et_2O (5 mL x 3). The organic layer was dried (Na_2SO_4), concentrated in vacuo, and the residue was purified by flash chromatography (Hex:EA/8:1) to provide **46** (68 mg, 85%) as a colorless oil. R_f = 0.70 (Hex:EA/6:1). $[\alpha]_D^{25}$ = +7 (*c* = 0.62, $CHCl_3$). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.26-6.76 (9H), 6.6 (br, 1H), 5.47 (br, 1H), 5.20-5.00 (3H), 4.25 (2H), 3.79 (s, 3H), 3.05-2.65 (2H), 1.73 (d, *J* = 2.0 Hz, 3H), 1.38 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 158.4, 138.5, 135.5, 133.4, 131.8, 129.3, 128.8, 128.7, 128.5, 128.3, 126.2, 115.4., 113.6, 79.7, 55.3, 54.8, 43.8, 40.7, 28.5, 19.7. HRMS (FAB) calcd for MH^+ ($C_{26}H_{34}NO_3$) 408.2538, found, 408.2528.

(2*S*, 3*Z*)-2-(N-4-Methoxybenzyl)-4-methyl-1-phenylhexa-3, 5-dien-2-ylamine (47). To a solution of **46** (40 mg, 0.098 mmol) in chloroform (0.4 mL), was added dropwise iodotrimethylsilane (16.8 μL, 0.118 mmol) and then the mixture was heated at 50 °C for 40 min. After cooling to rt, MeOH (75 μL) was added and the solvent was evaporated in vacuo. Then Et_2O (0.5 mL) and acetic acid (30%, 0.5 mL) were added and stirring was continued for 10 min. The solution was basified by sat. Na_2CO_3 to pH = 9 and then extracted with Et_2O (5 mL x 3). The organic layer was washed with brine (3 mL) and dried (Na_2SO_4). After evaporation of the solvent, the crude product **47** (16 mg, 53%) was used in the following reaction without further purification. $[\alpha]_D^{25}$ = +6 (*c* = 1.40, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-6.78 (9H), 6.57 (dd, *J* = 17.2, 10.4 Hz, 1H), 5.29 (d, *J* = 9.2 Hz, 1H), 5.20 (dq, *J* = 17.2, 0.8 Hz, 1H), 5.04 (dq, *J* = 11.2, 1.6 Hz, 1H), 3.83-3.77 (m, 1H), 3.78 (s, 3H), 3.71 and 3.51 (ABq, *J* = 13.6 Hz, 2H), 2.79-2.68 (2H), 1.86 (d, *J* = 1.2 Hz, 3H), 1.7 (br, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 138.8, 134.6, 133.9, 133.7, 132.7, 129.6, 129.4, 128.6, 126.5, 114.7, 113.9, 55.5, 55.1, 50.9, 42.7, 20.1. HRMS (FAB) calcd for MH^+ ($C_{21}H_{26}NO$) 308.2014, found, 308.2021.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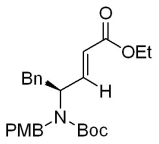
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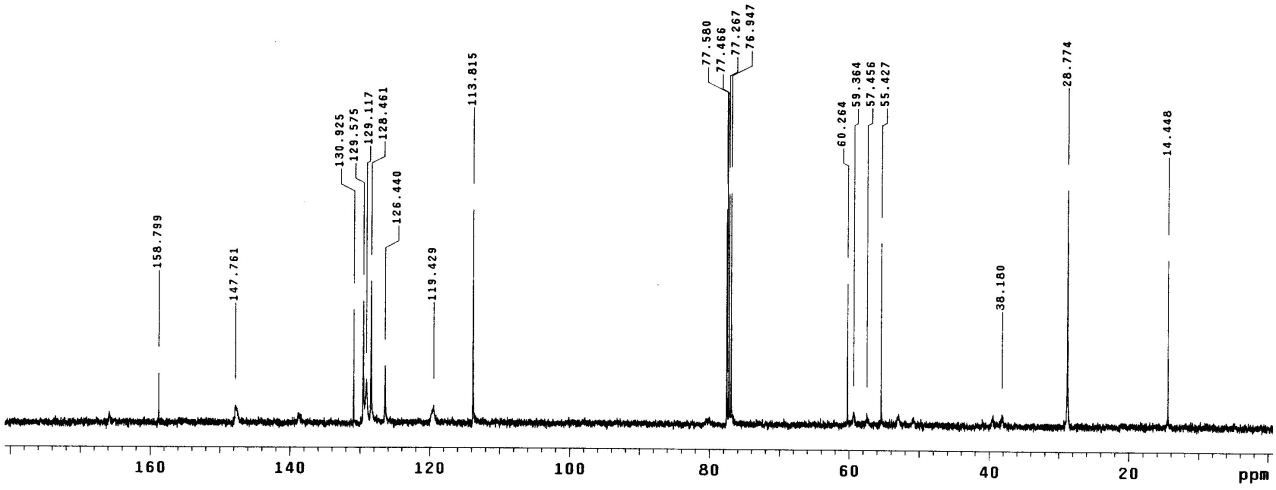
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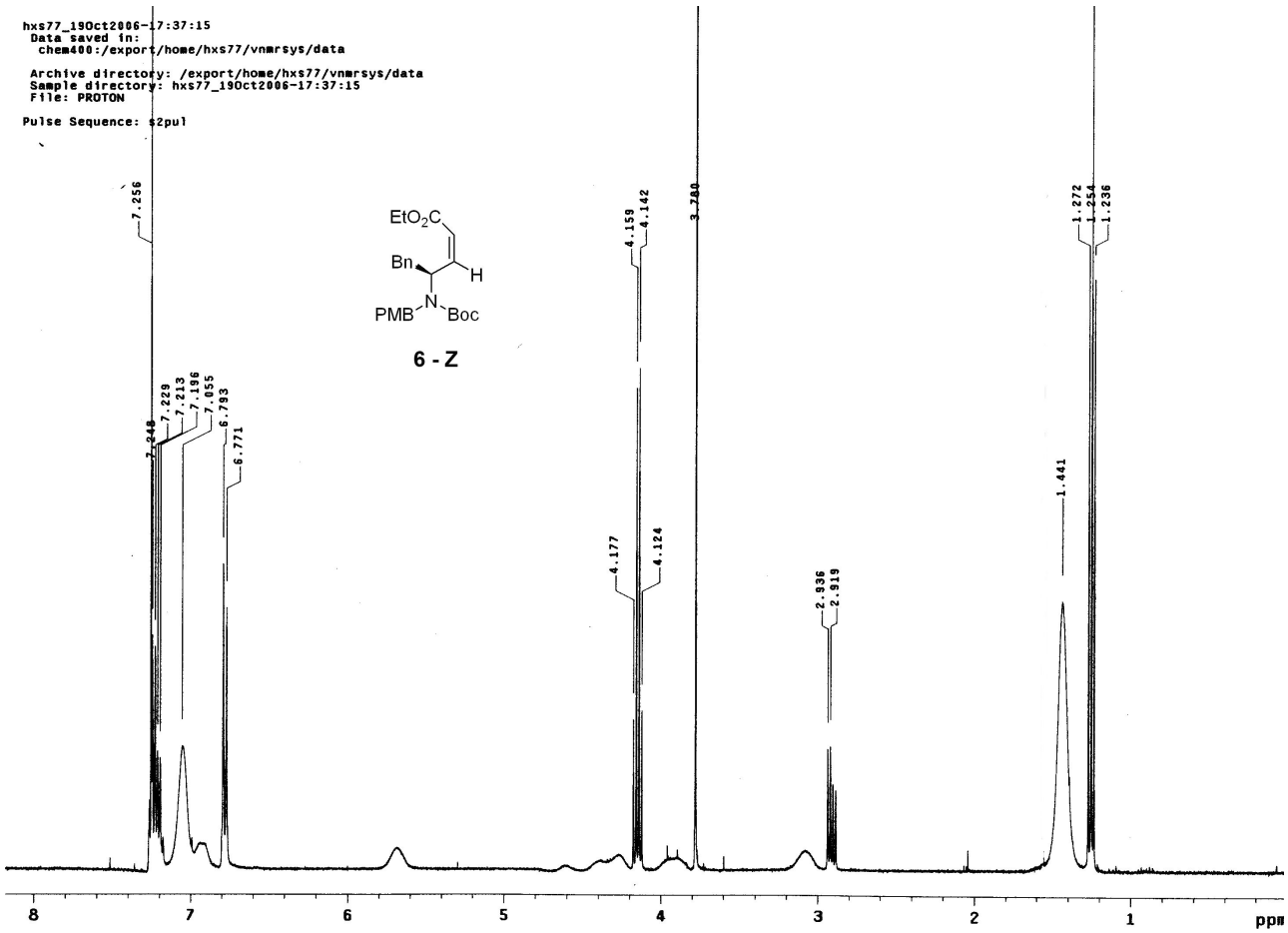
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Boc
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6.771
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4.142
4.177
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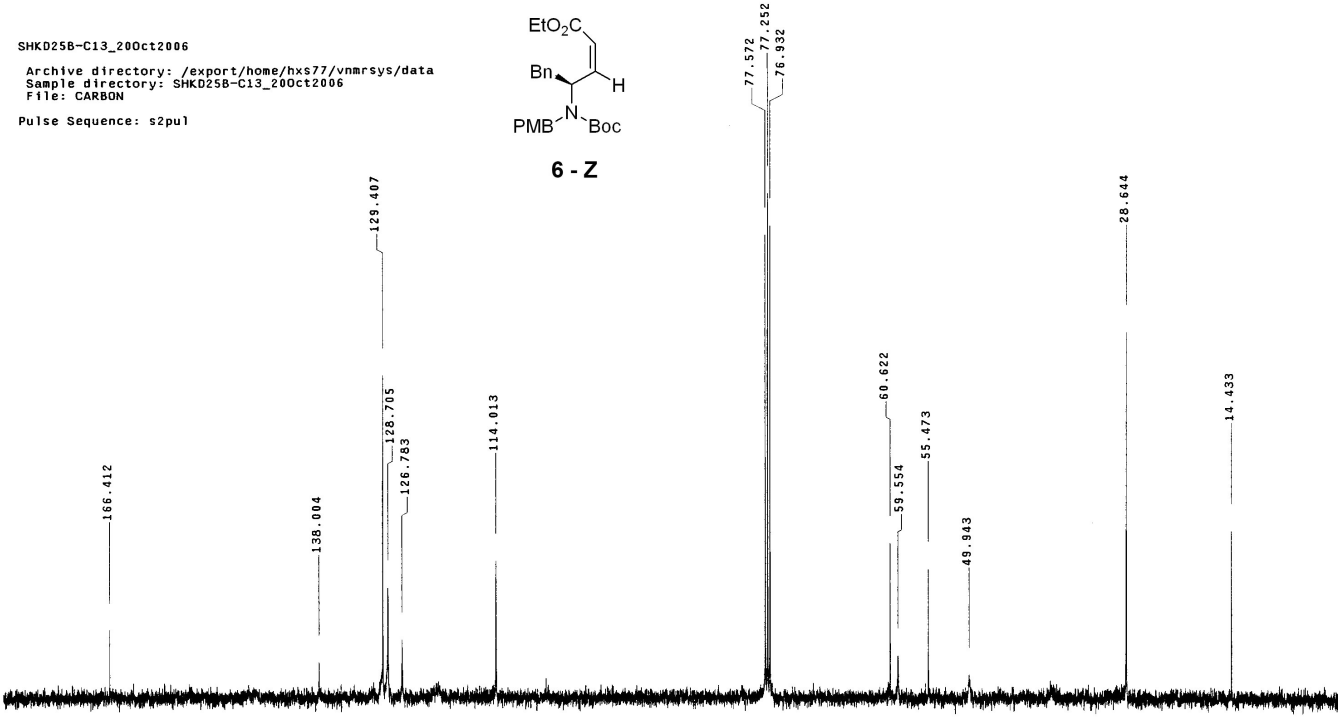
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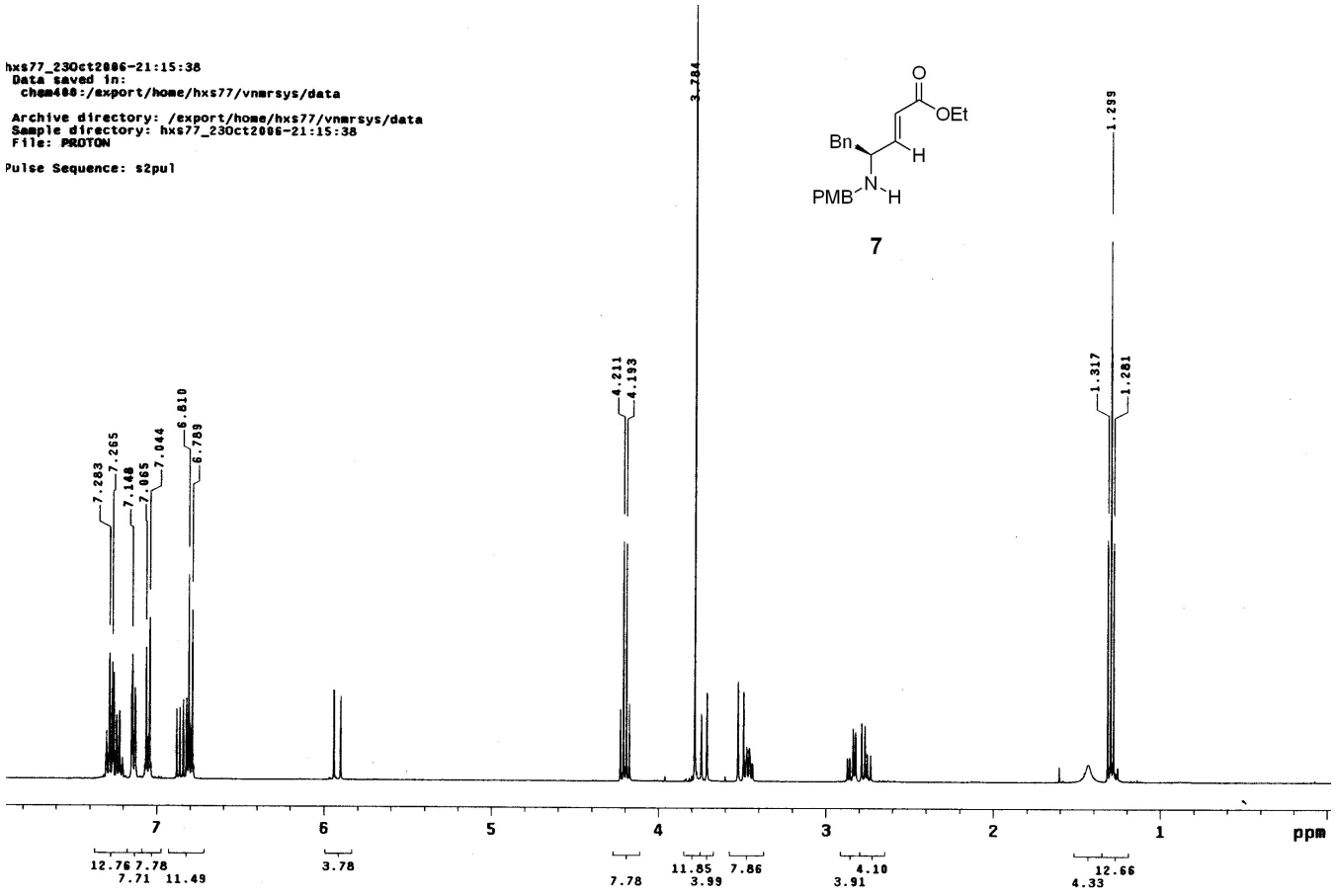
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1.281
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Bn
H
PMB
N
H
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ppm
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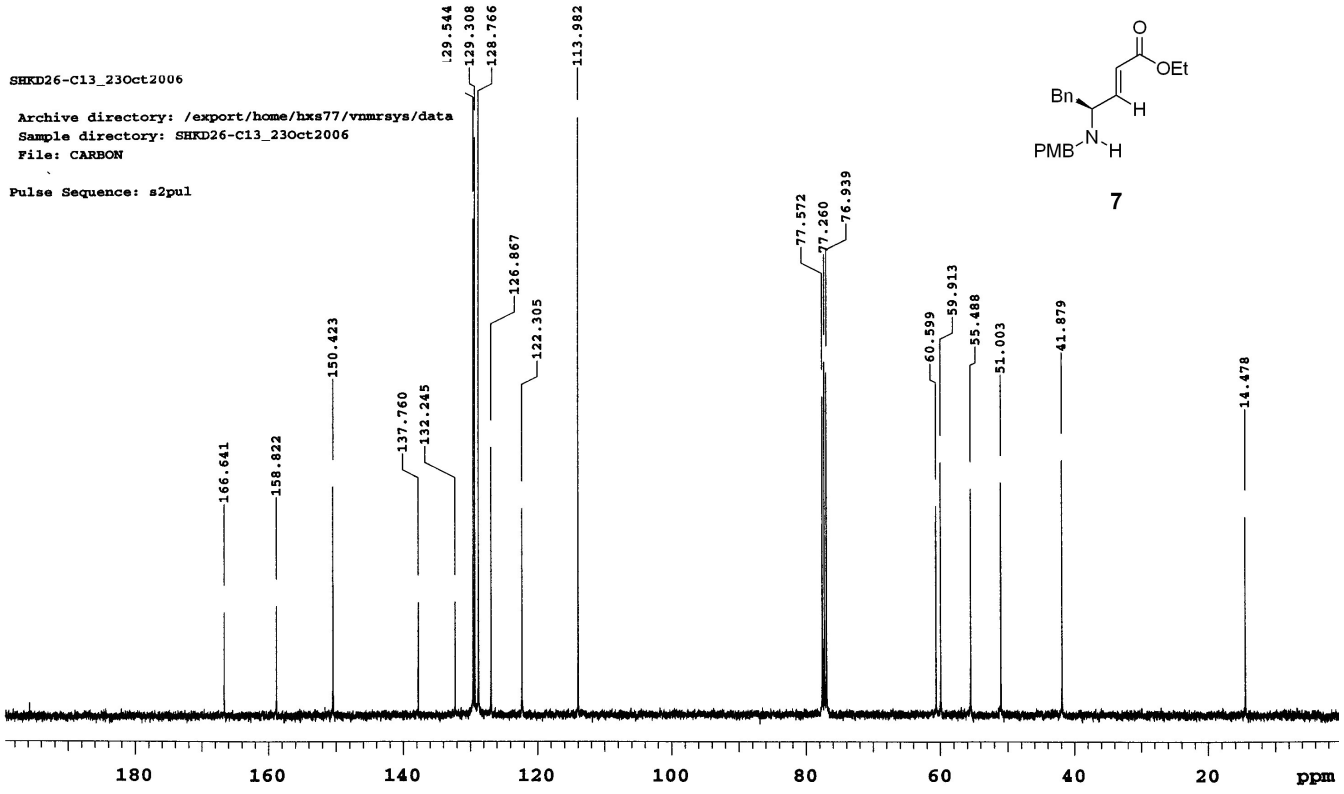
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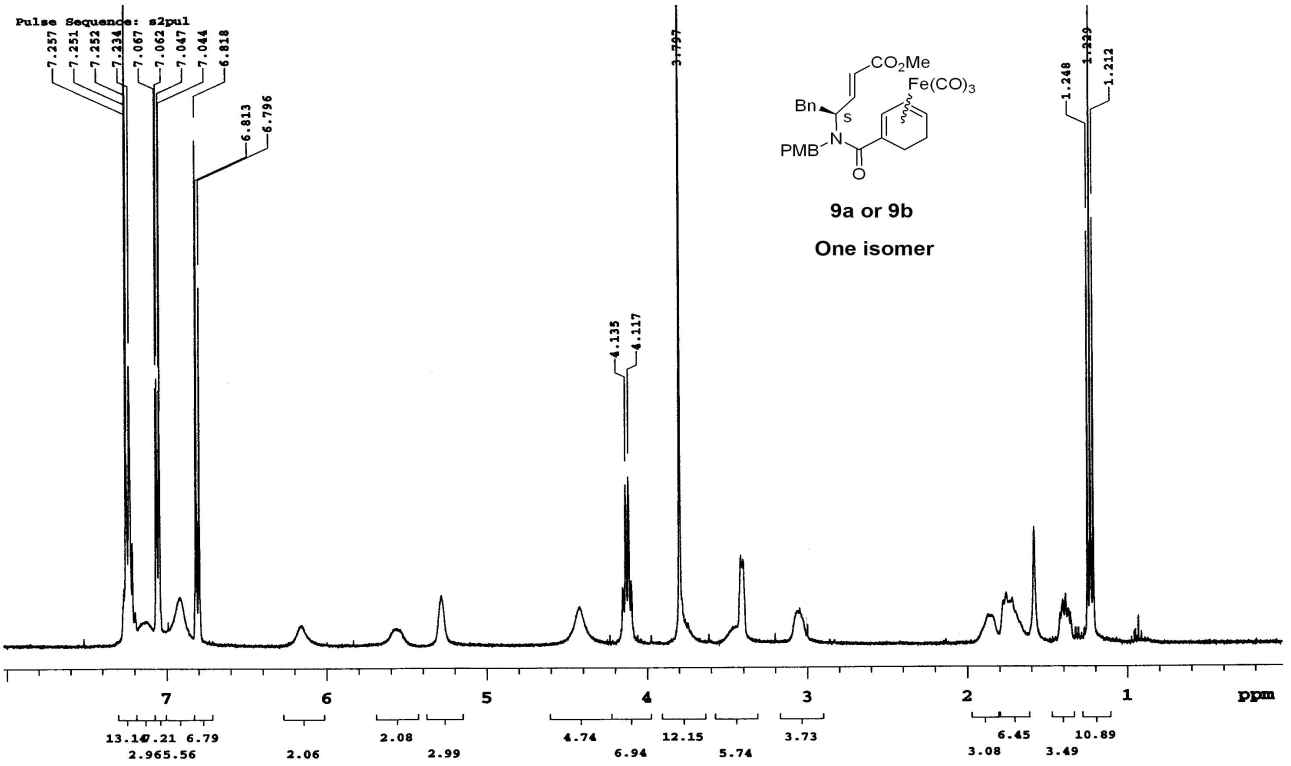
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S
PMB
N
O
9a or 9b
One isomer
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6
5
4
3
2
1
ppm
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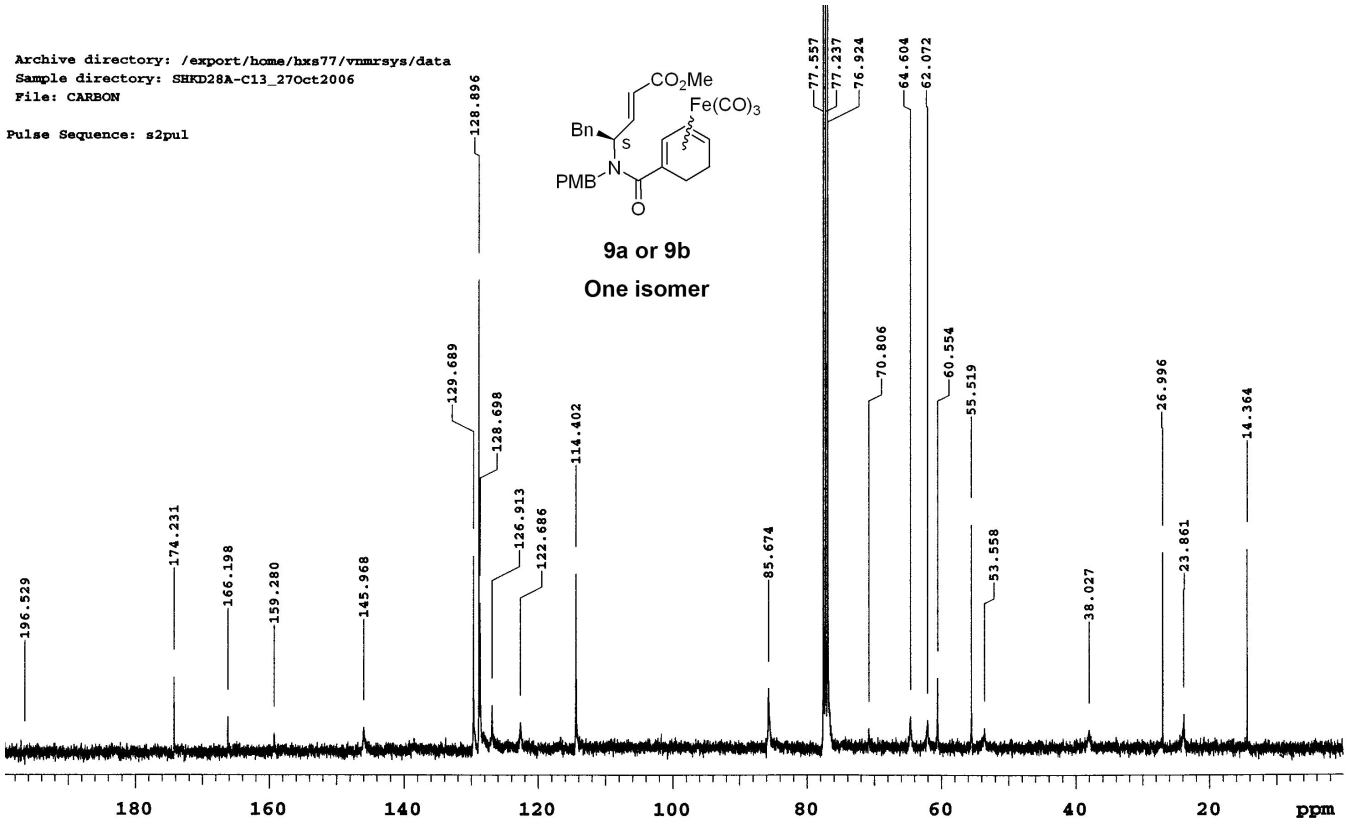
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129.689
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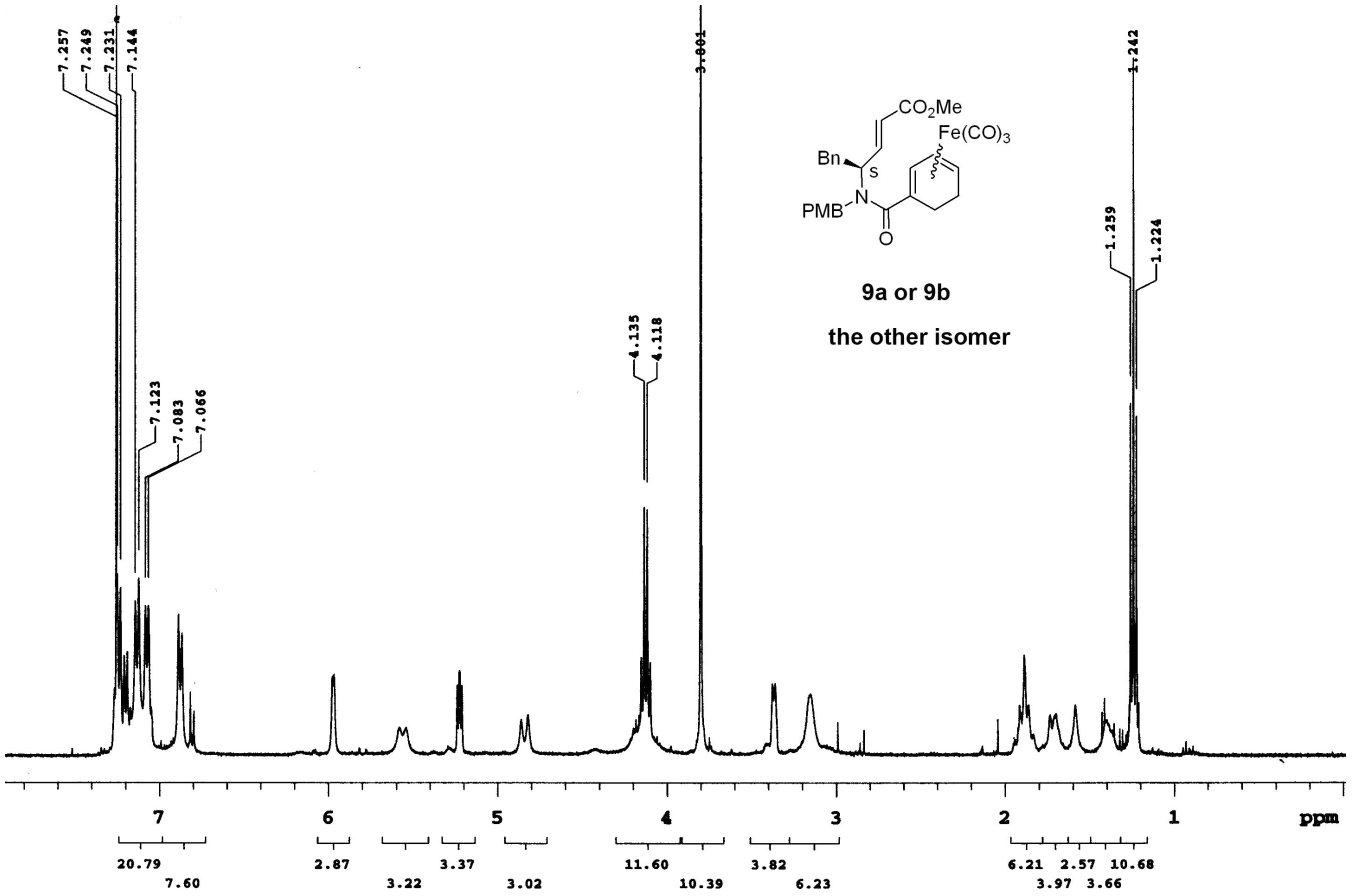
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N
PMB
O
9a or 9b
the other isomer
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6
5
4
3
2
1
ppm
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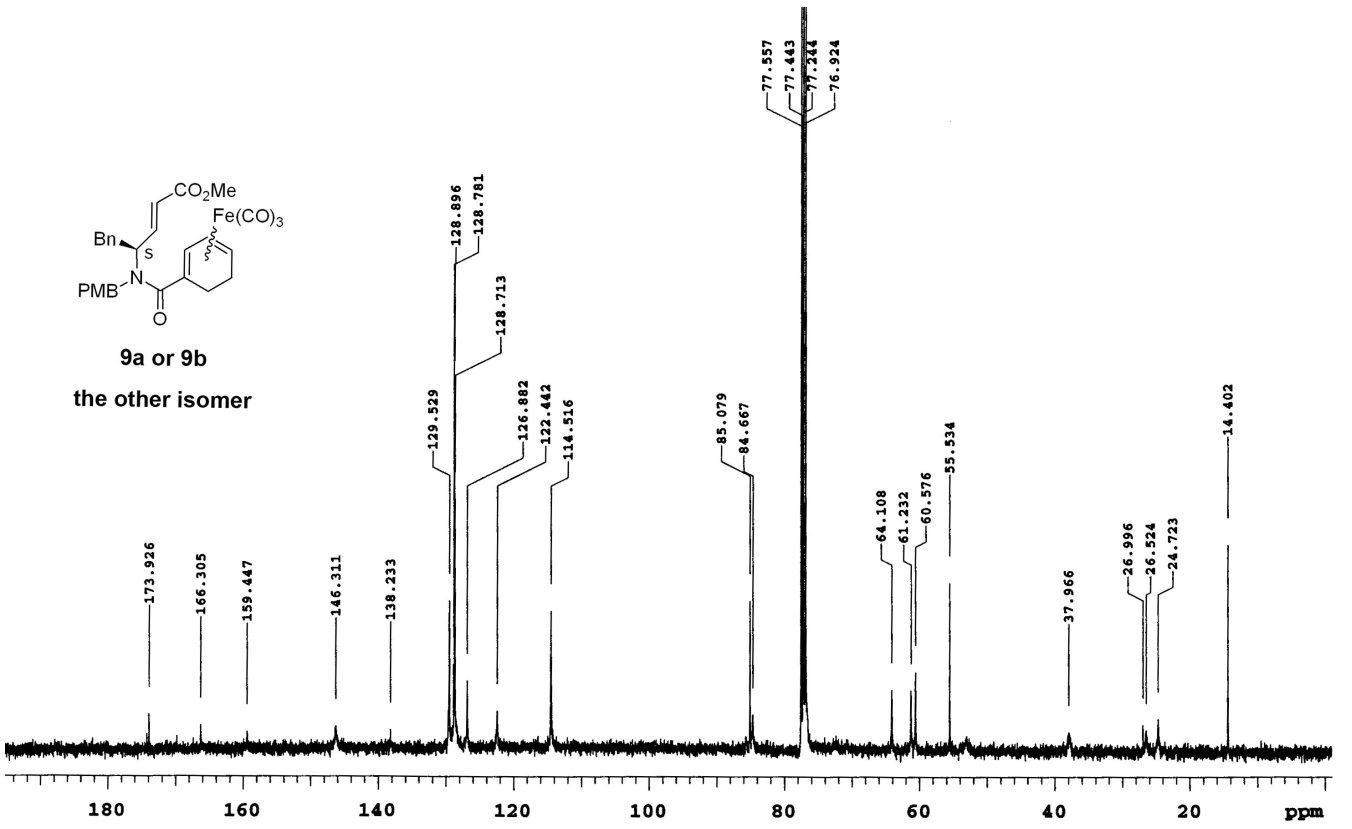
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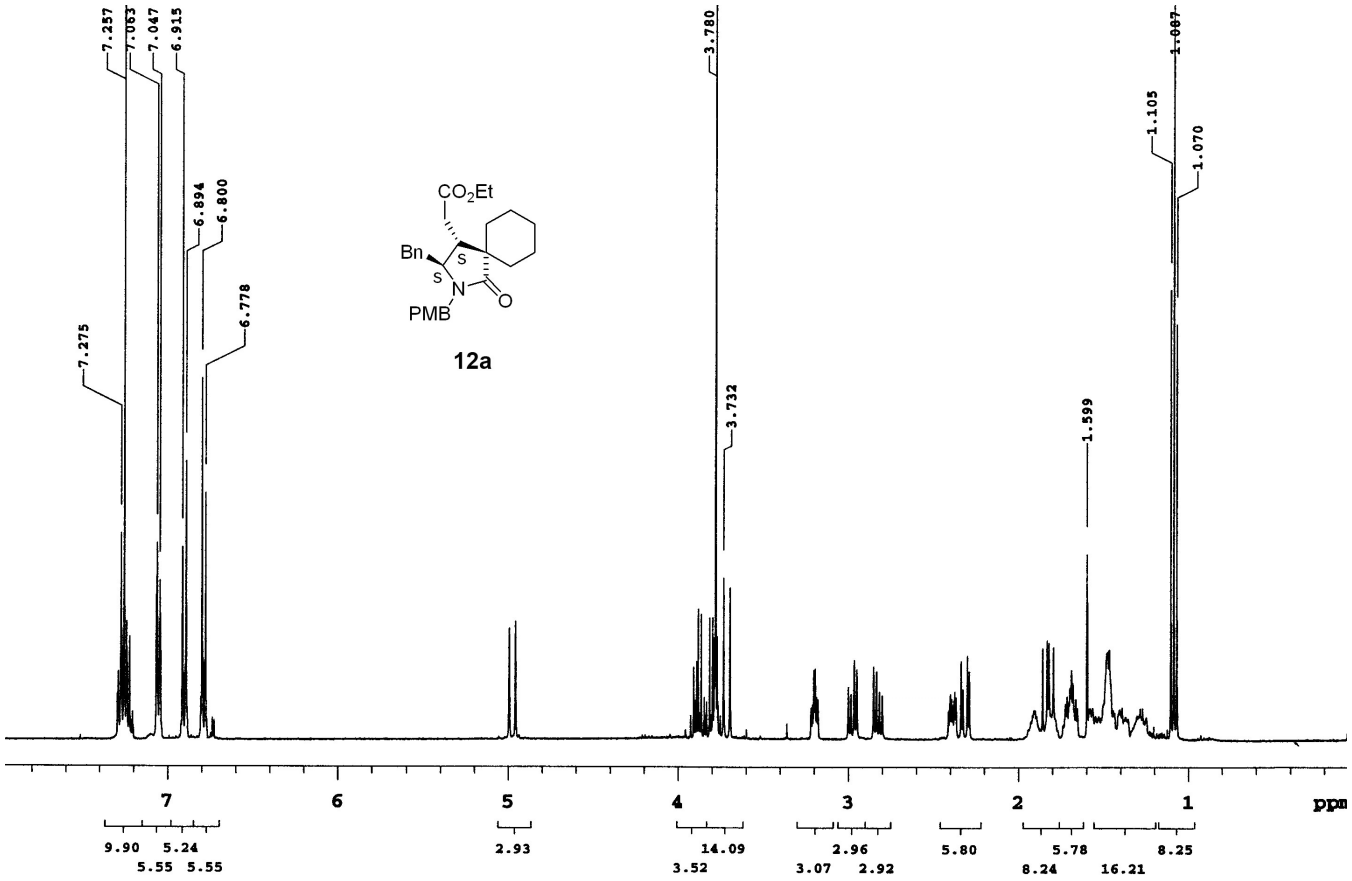
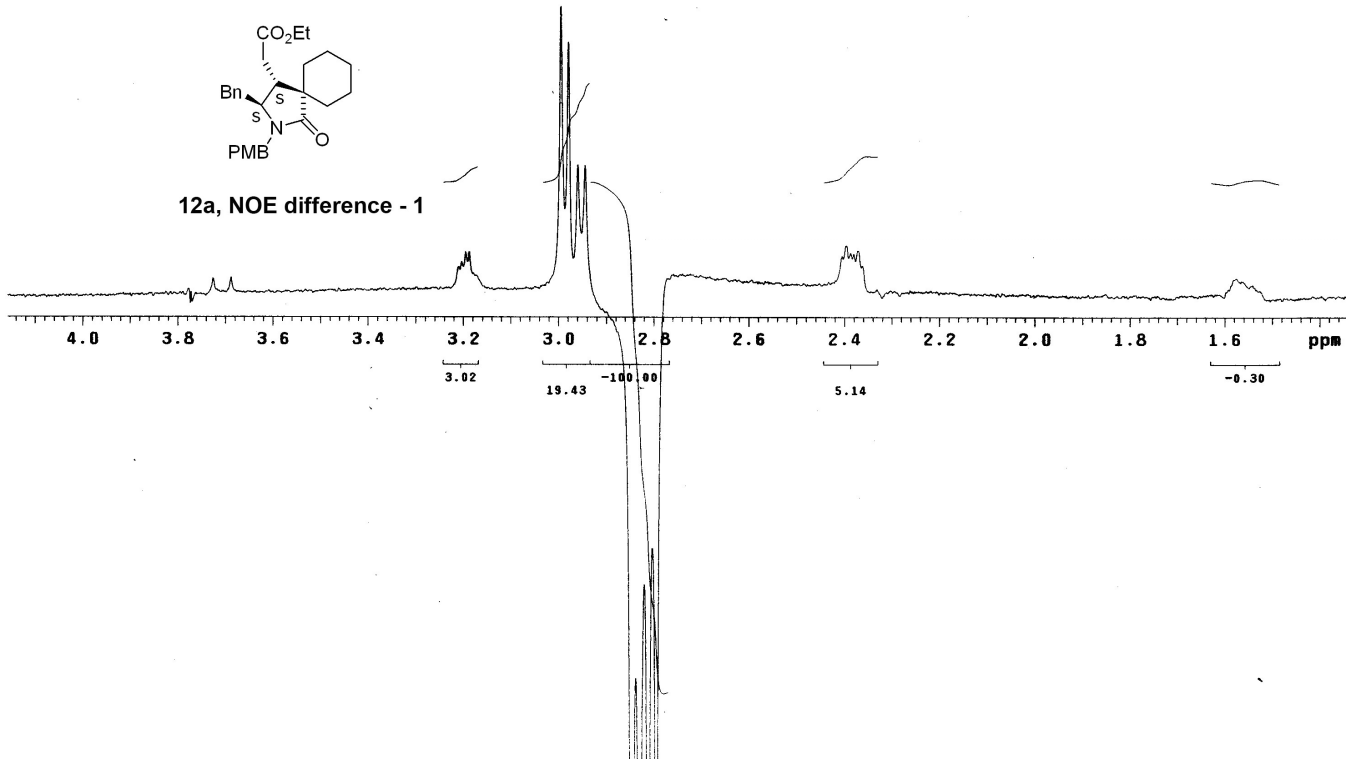
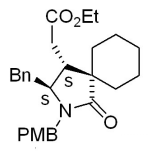
20
ppm

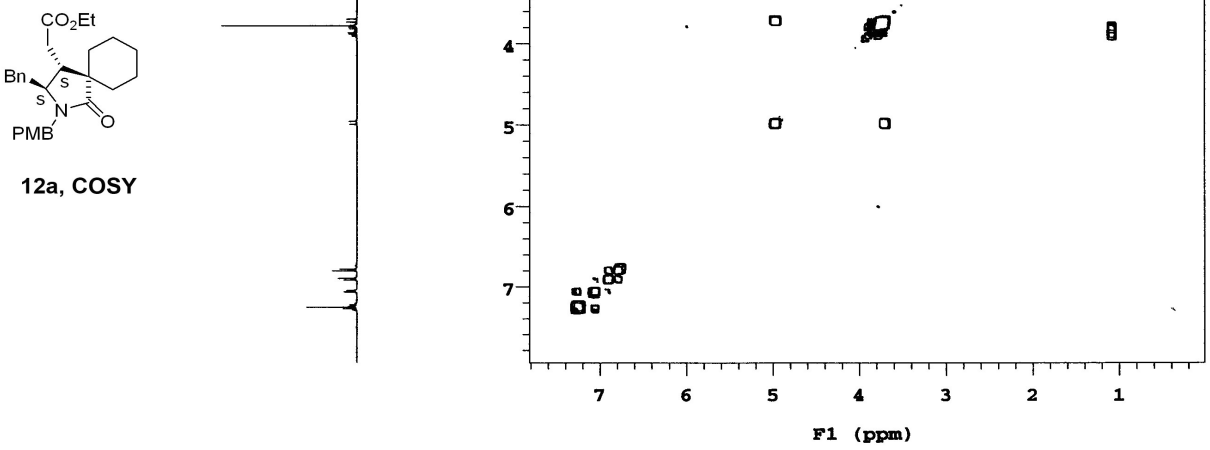

7.257
7.063
7.047
6.915
6.894
6.800
6.778
7.275
3.780
3.732
1.599
1.105
1.087
1.070
CO2Et
Bn
S
S
N
O
PMB
12a
7
6
5
4
3
2
1
ppm
9.90
5.24
5.55
5.55
2.93
14.09
3.52
2.96
3.07
2.92
5.80
5.78
8.24
8.25
16.21


CO2Et
Bn
S
S
N
O
PMB
12a, NOE difference - 1
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
ppm
3.02
19.43
-100.00
5.14
-0.30

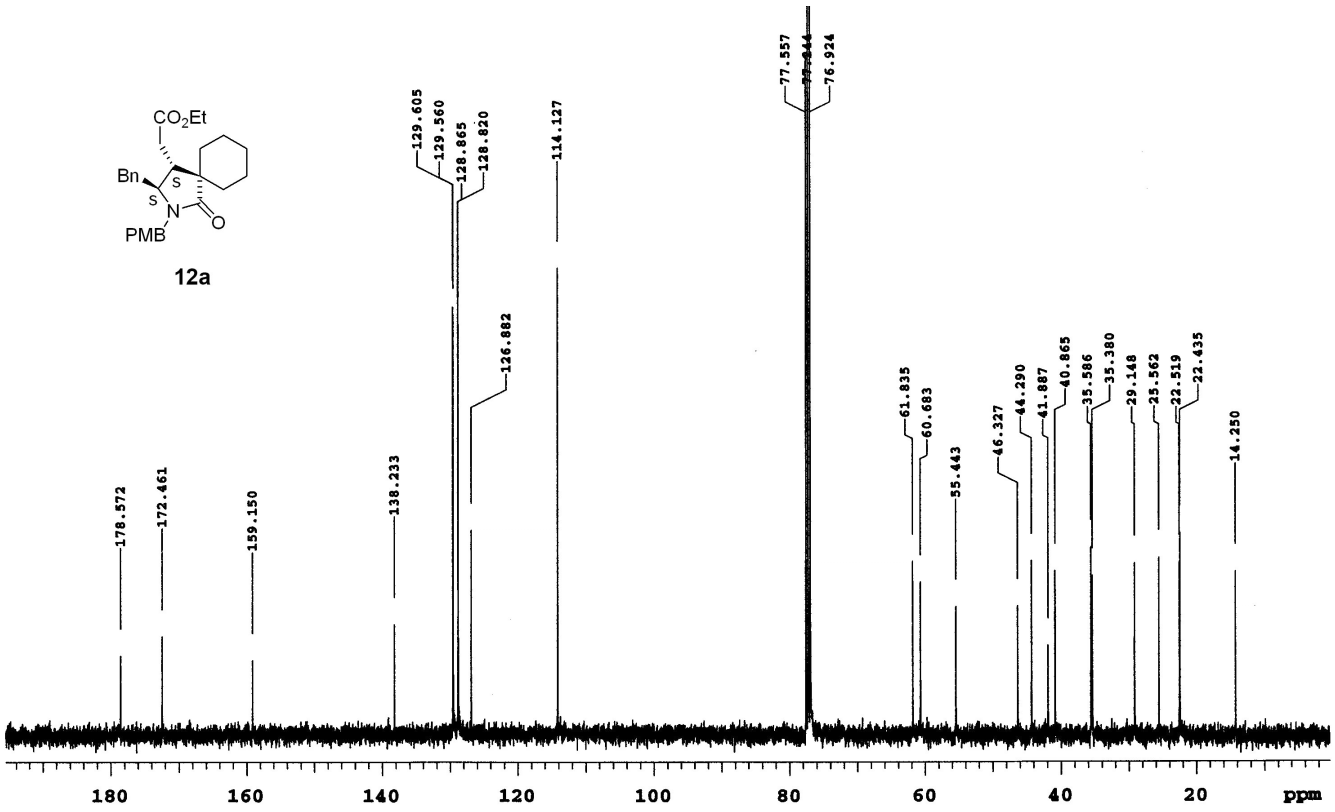


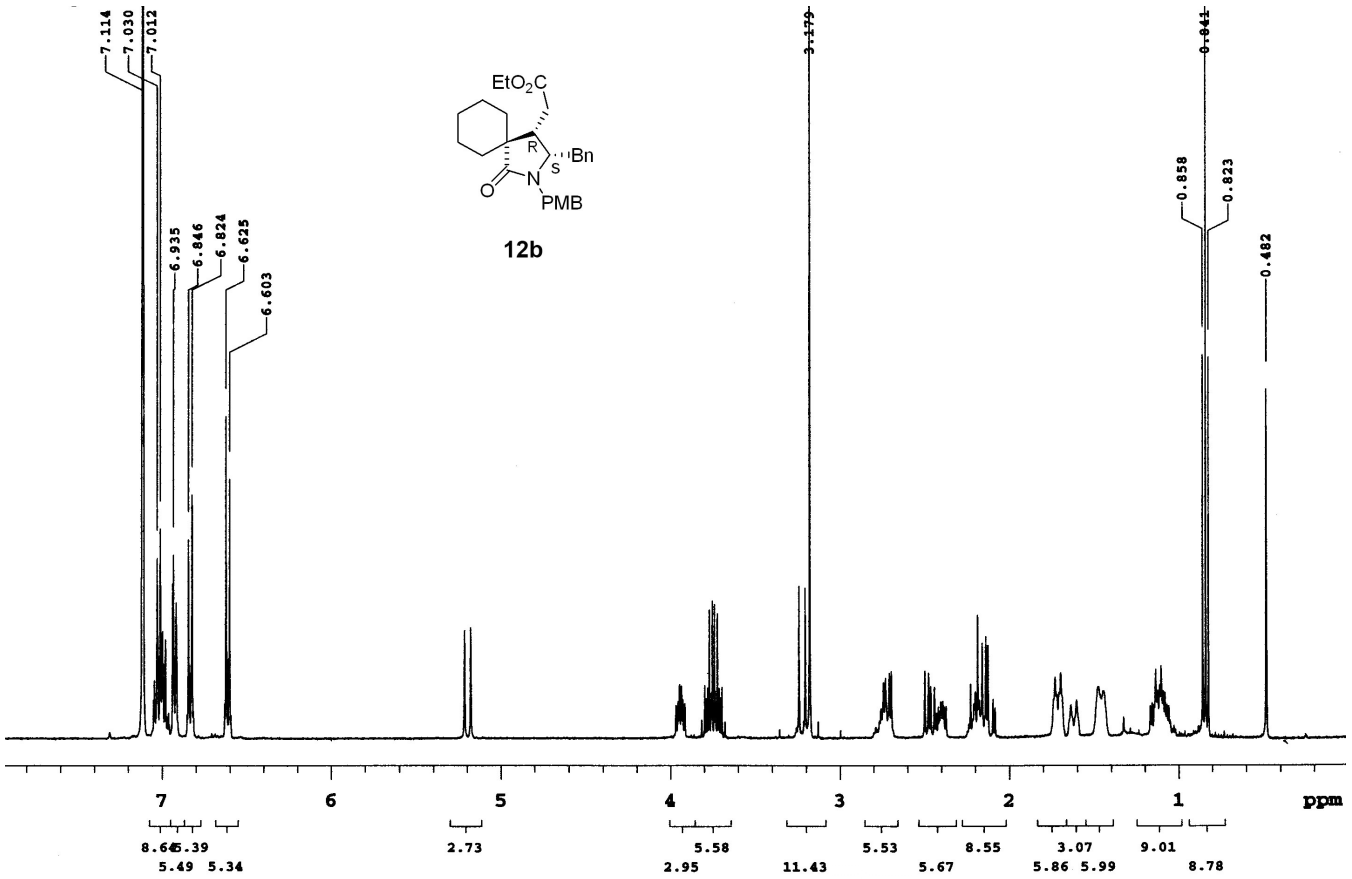
12a NOE difference - 2

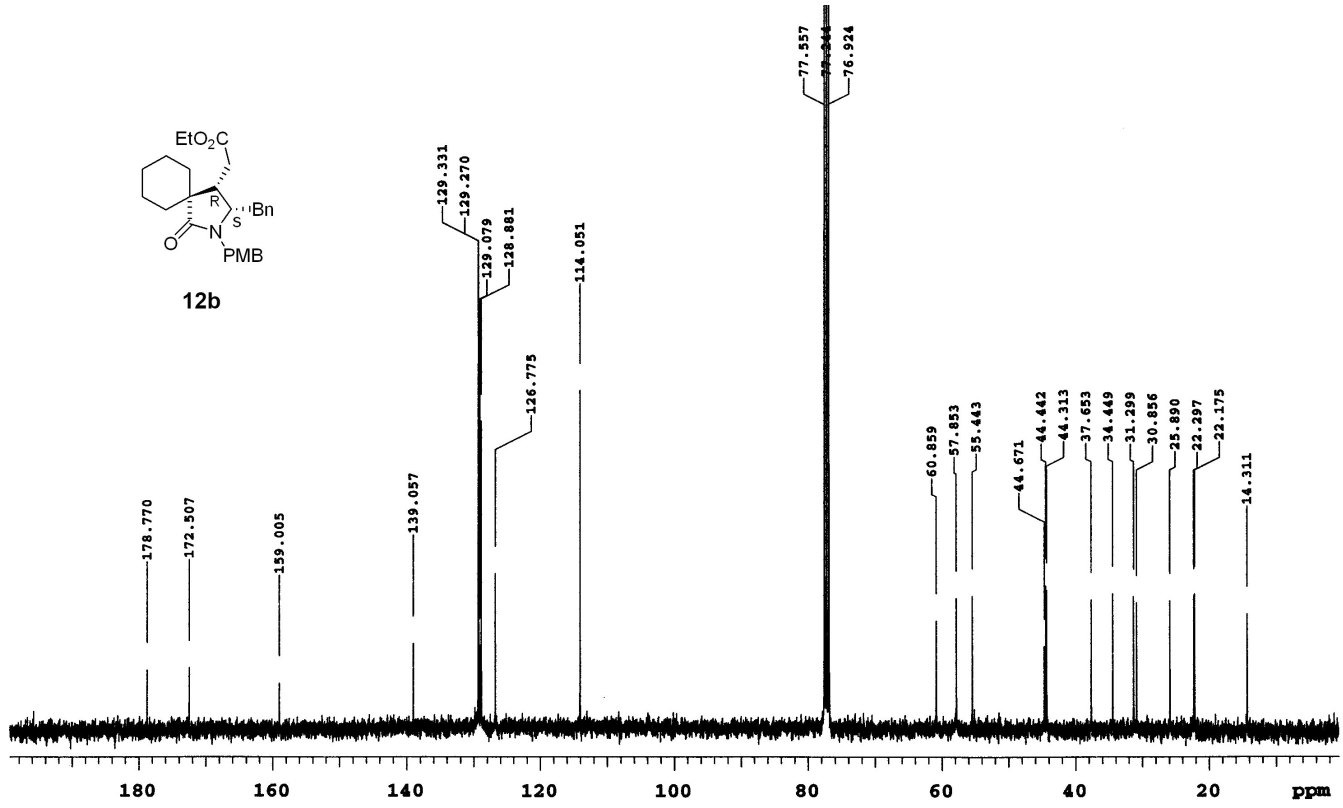

```
Pulse Sequence: gCOSY
 Solvent: CDCl3
 Ambient temperature
INOVA-400  "chem400"

 Relax. delay 1.000 sec
 Acq. time 0.160 sec
 Width     6395.9 Hz
 2D Width 6395.9 Hz
 Single scan
 128 increments
OBSERVE    H1, 399.7467337 MHz
DATA PROCESSING
 Sq. sine bell 0.080 sec
F1 DATA PROCESSING
 Sq. sine bell 0.020 sec
FT size 2048 x 2048
Total time 2 min, 50 sec
```

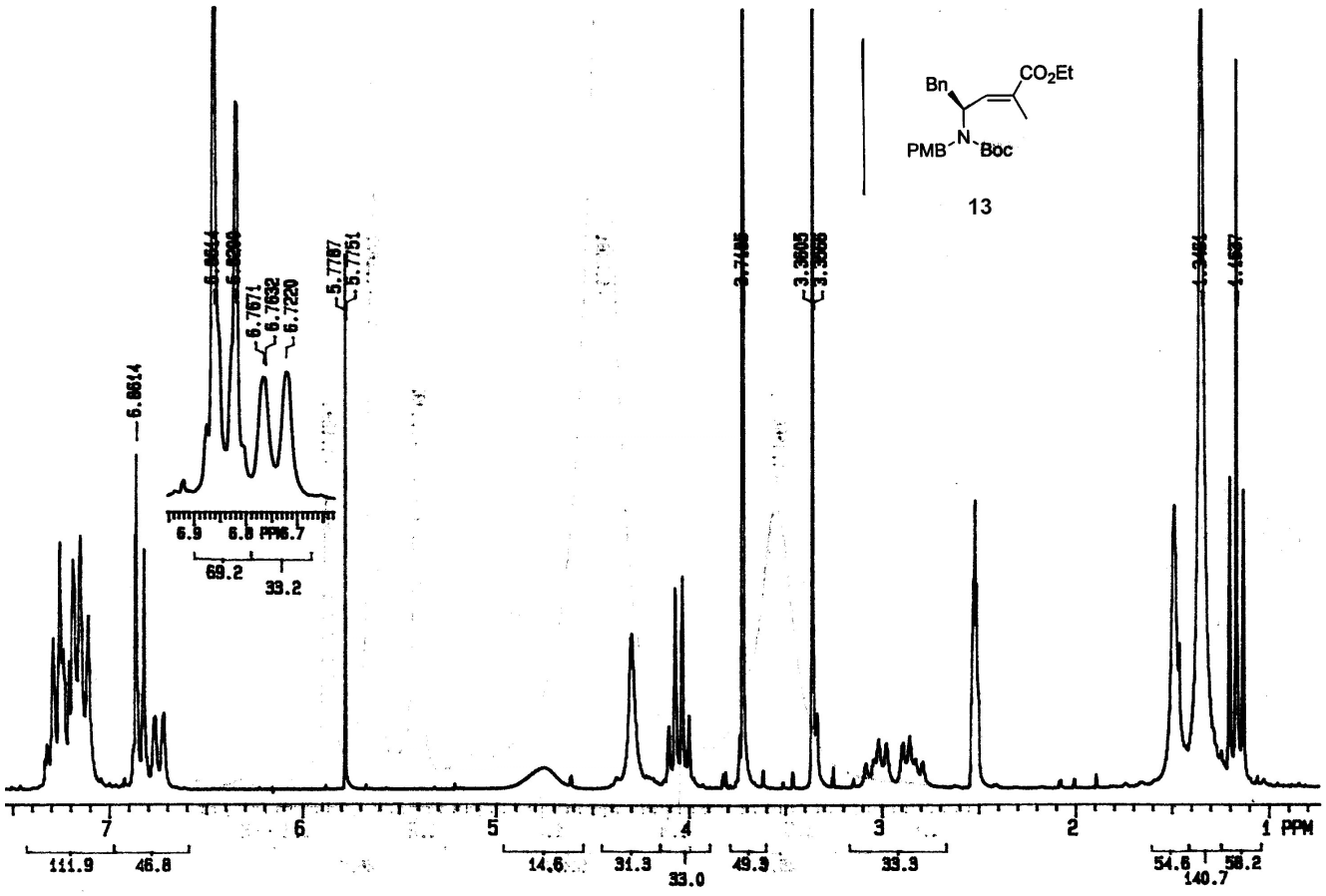


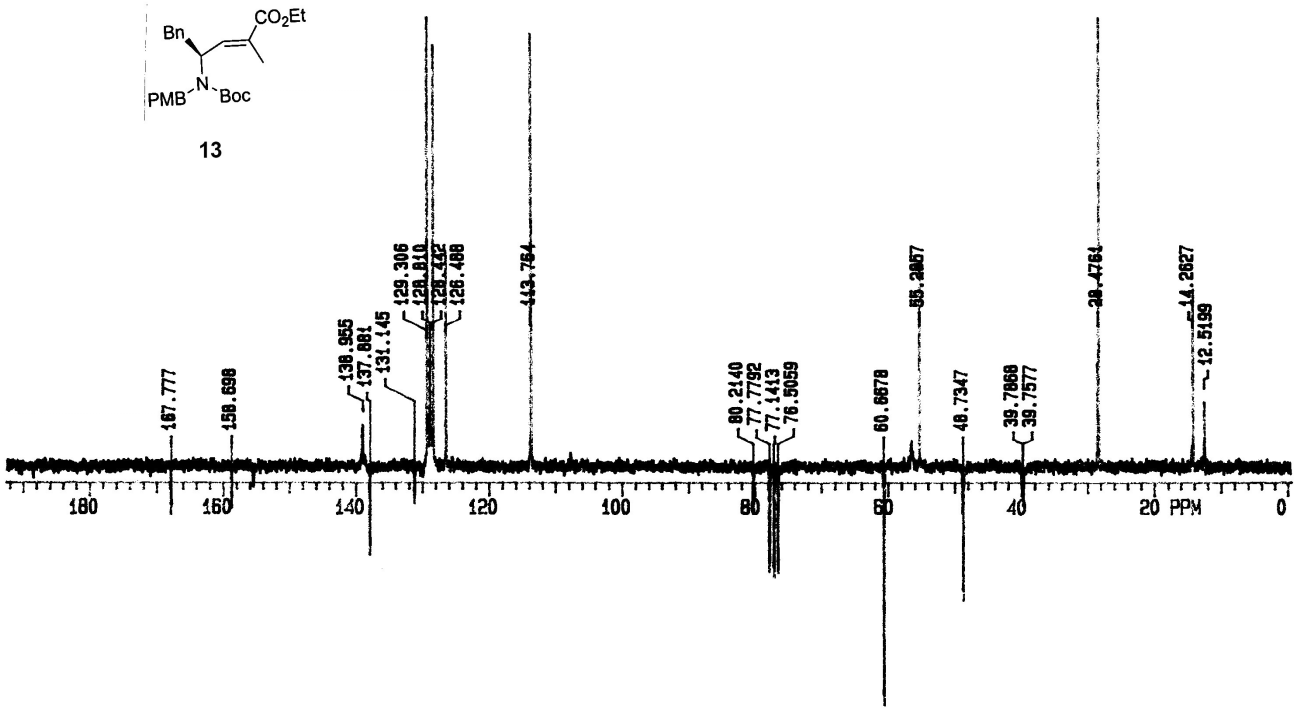
12a, COSY

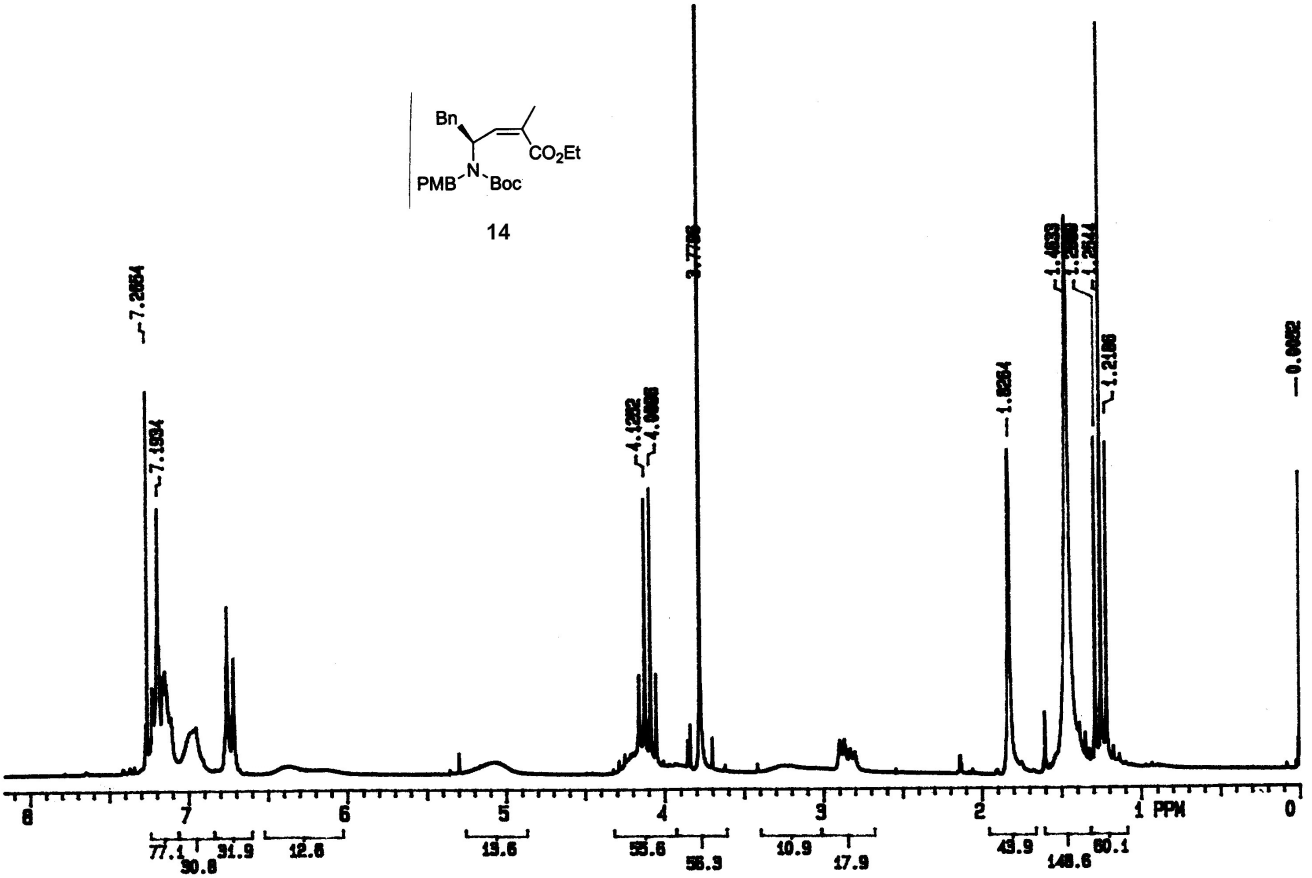

CO2Et
Bn
S
S
N
O
PMB
12a
178.572
172.461
159.150
138.233
129.605
129.560
128.865
128.820
126.882
114.127
77.557
77.244
76.924
61.835
60.683
55.443
46.327
44.290
41.887
40.865
35.586
35.380
29.148
25.562
22.519
22.435
14.250
180
160
140
120
100
80
60
40
20
ppm

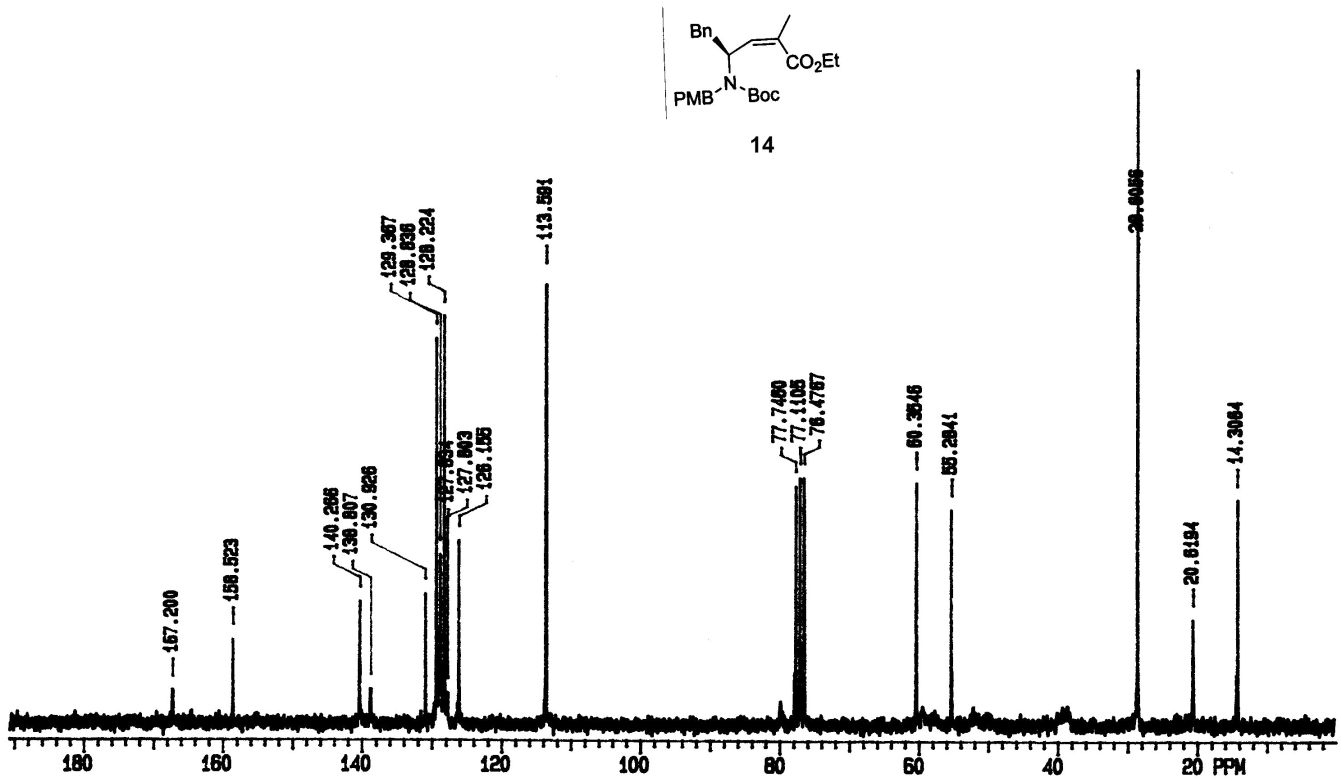

7.114
7.030
7.012
6.935
6.846
6.824
6.625
6.603
EtO2C
R
S
Bn
O
N
PMB
12b
3.179
0.841
0.858
0.823
0.482
7
6
5
4
3
2
1
ppm
8.64
5.39
5.49
5.34
2.73
5.58
2.95
11.43
5.53
5.67
8.55
3.07
5.86
5.99
9.01
8.78

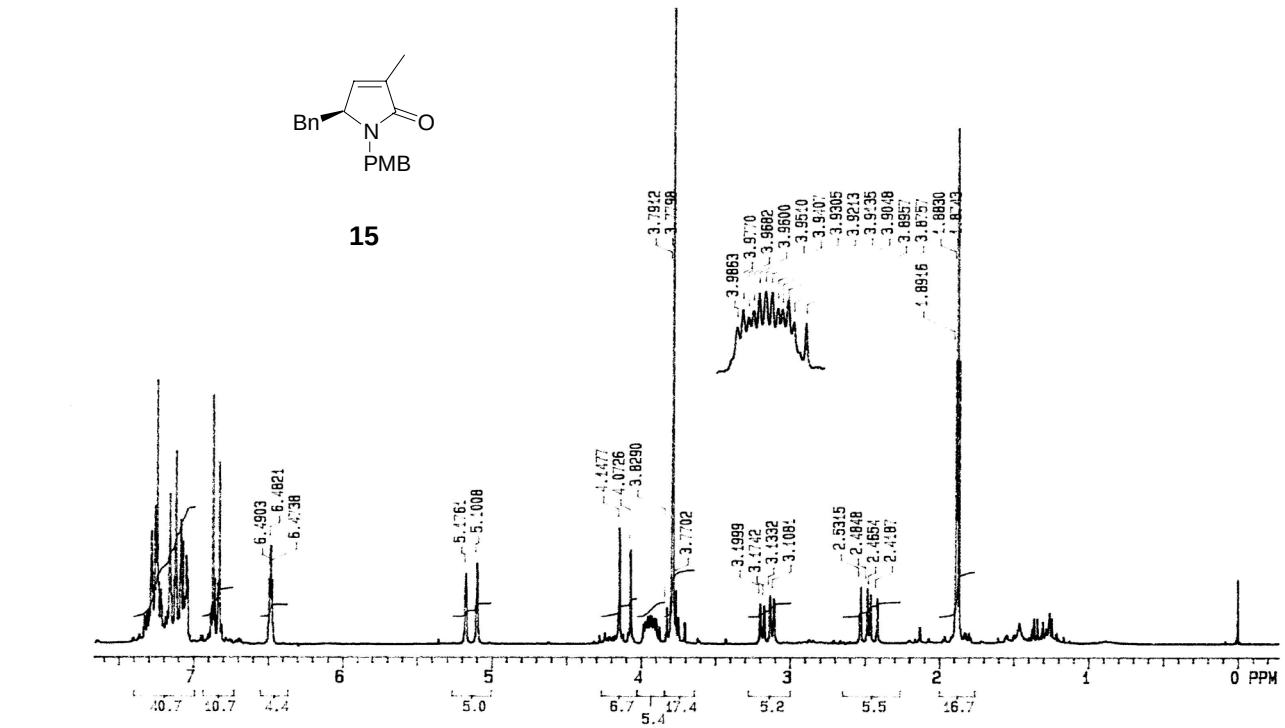

EtO2C
R
S
Bn
N
PMB
O
12b
178.770
172.507
159.005
139.057
129.331
129.270
129.079
128.881
126.775
114.051
77.557
76.924
60.859
57.853
55.443
44.671
44.442
44.313
37.653
34.449
31.299
30.856
25.890
22.297
22.175
14.311
180
160
140
120
100
80
60
40
20
ppm

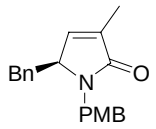

Bn
CO2Et
PMB
N
Boc
13
6.8614
6.7671
6.7632
6.7220
5.7787
5.7751
3.3905
6.9
6.8 PPM6.7
69.2
33.2
7
6
5
4
3
2
1 PPM
111.9
46.8
14.6
31.3
33.0
49.9
33.9
54.6
58.2
140.7


Bn
CO2Et
PMB
N
Boc
13
167.777
158.698
136.955
137.881
131.145
129.306
126.486
113.784
80.2140
77.7792
77.1413
76.5059
60.6678
55.2657
48.7347
39.7868
39.7577
28.4764
14.2627
12.5199
180
160
140
120
100
80
60
40
20 PPM
0

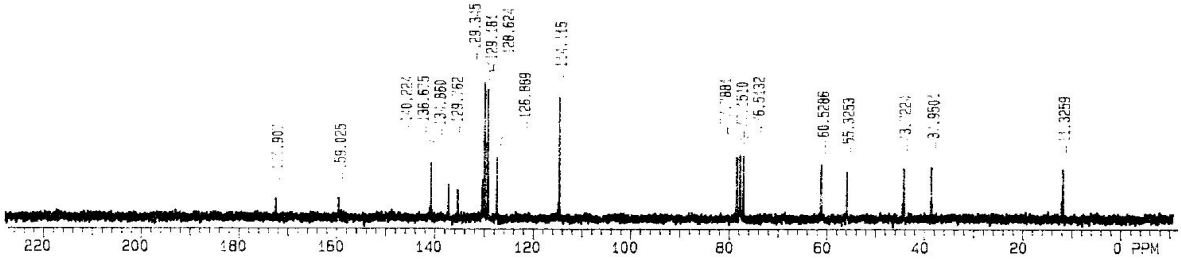

Bn
CO2Et
PMB
N
Boc
14
7.2654
7.1934
4.1232
4.0988
3.7736
1.8264
1.4033
1.2644
1.2186
0.0052
8
7
6
5
4
3
2
1 PPM
0
77.1
30.8
31.9
12.6
15.6
55.6
55.9
10.9
17.9
43.9
148.6
60.1

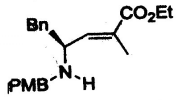

Bn
CO2Et
PMB
N
Boc
14
167.200
158.823
140.266
138.807
130.926
129.367
128.836
128.224
127.803
126.155
113.591
77.7460
77.1105
76.4767
60.3546
55.2941
29.8056
20.8194
14.3064
180
160
140
120
100
80
60
40
20 PPM


Bn
N
O
PMB
15
7
6
5
4
3
2
1
0 PPM
10.7
4.4
5.0
6.7
17.4
5.4
5.2
5.5
16.7


Bn
N
O
PMB

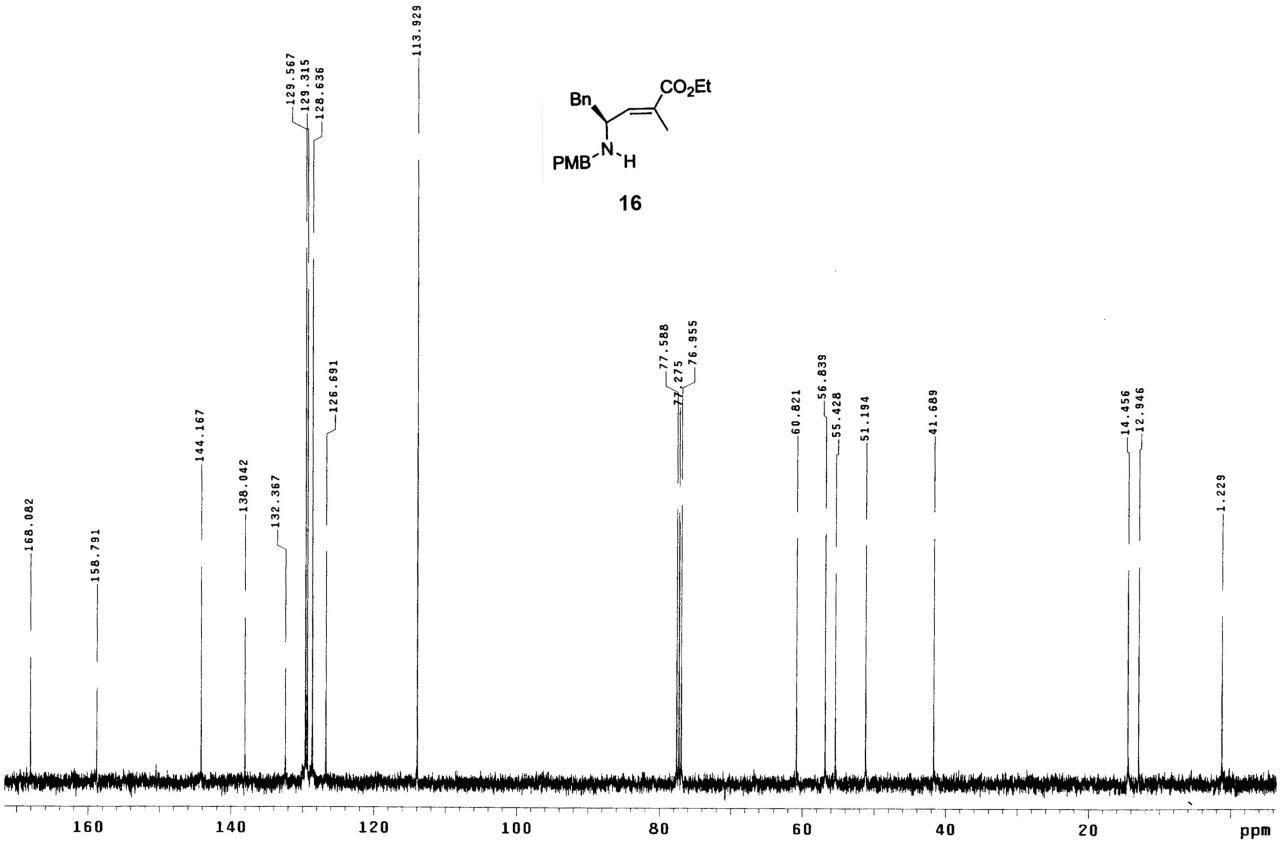
15

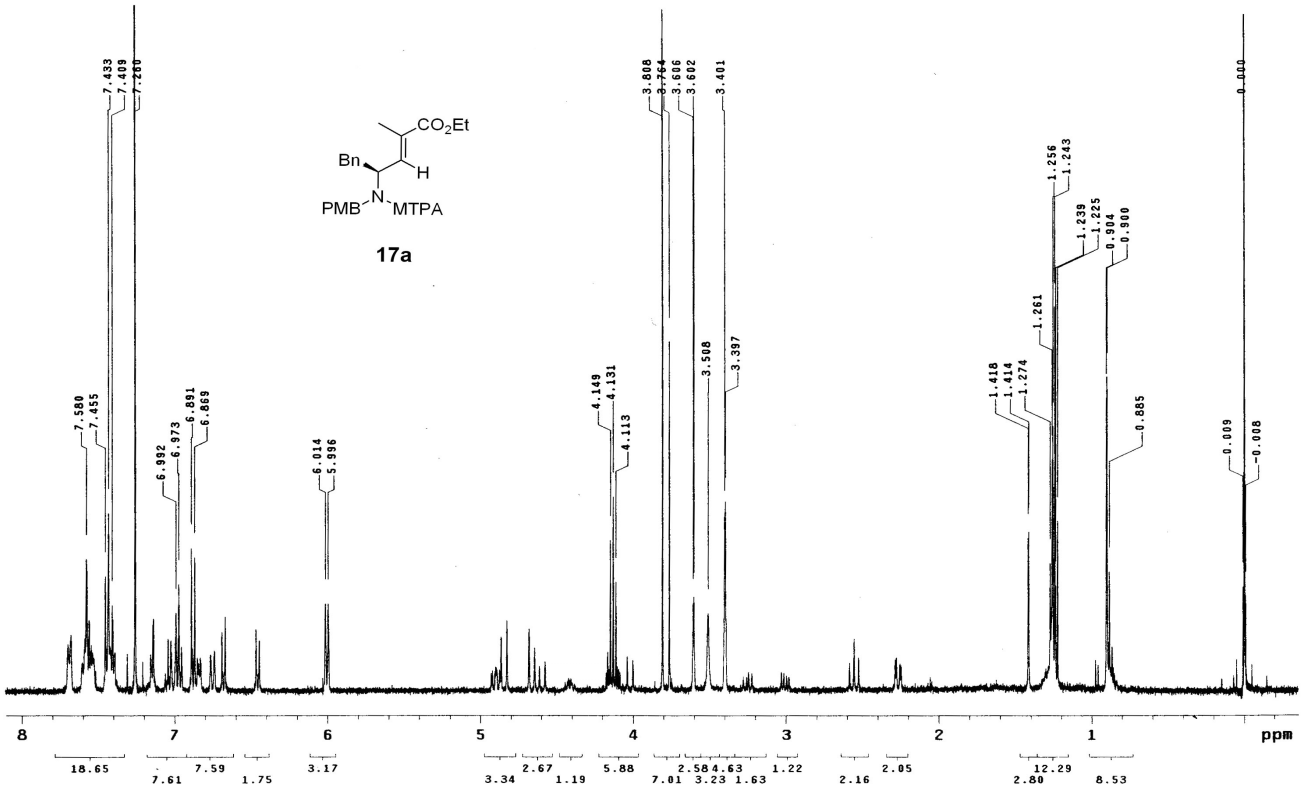

220
200
180
160
140
120
100
80
60
40
20
0 PPM

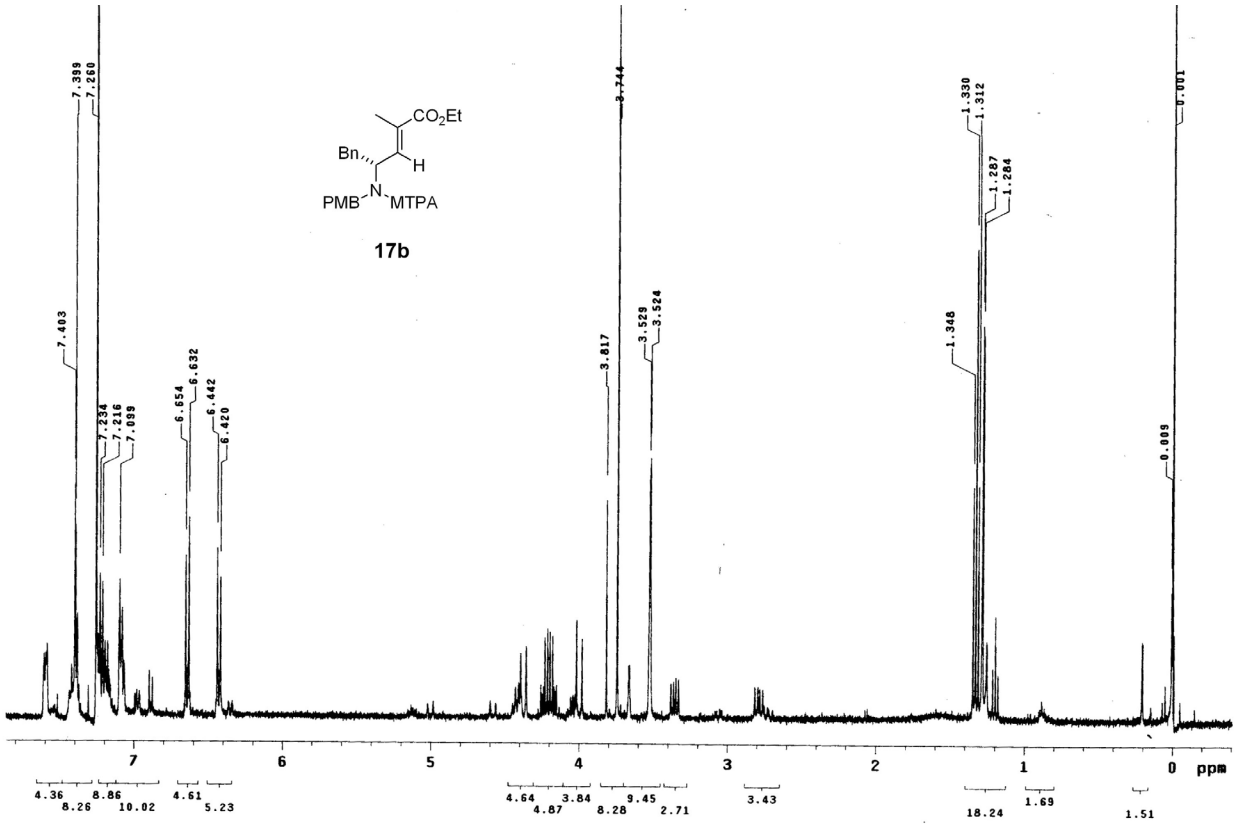

Bn
CO2Et
PMB
N
H

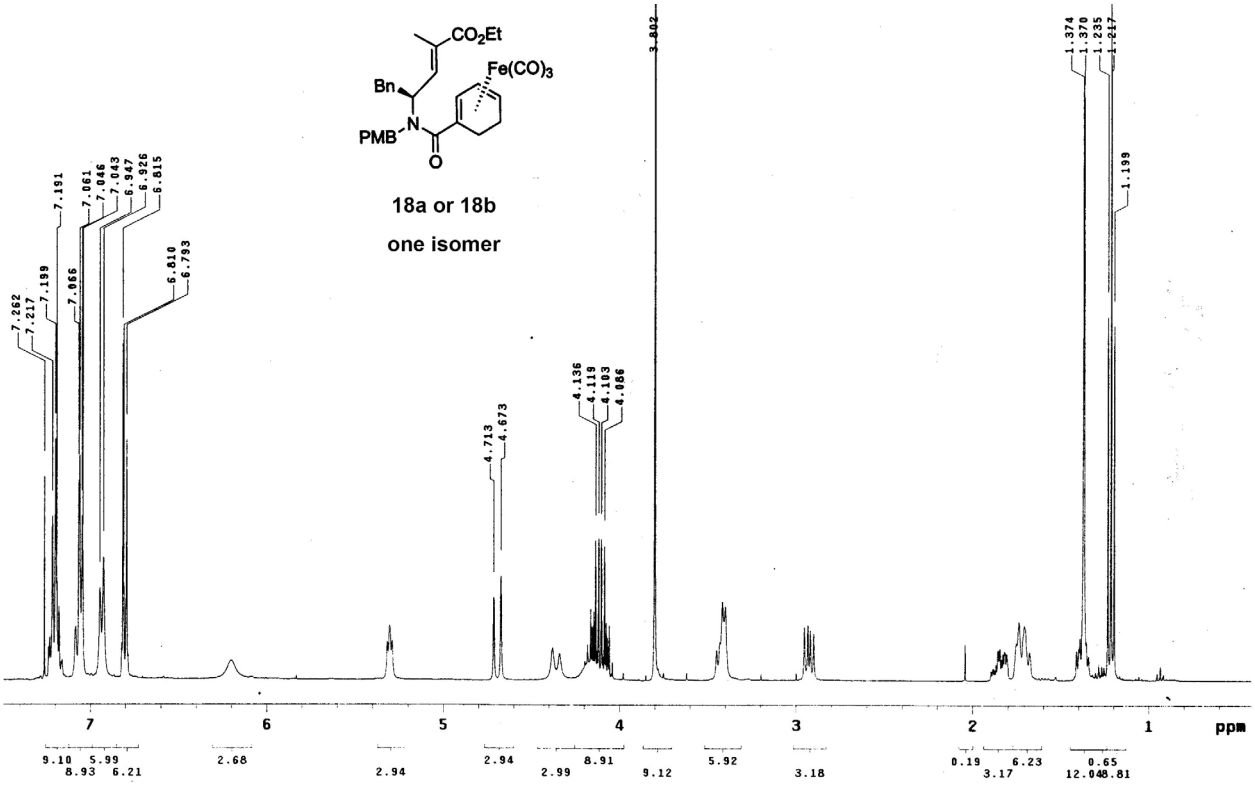
16

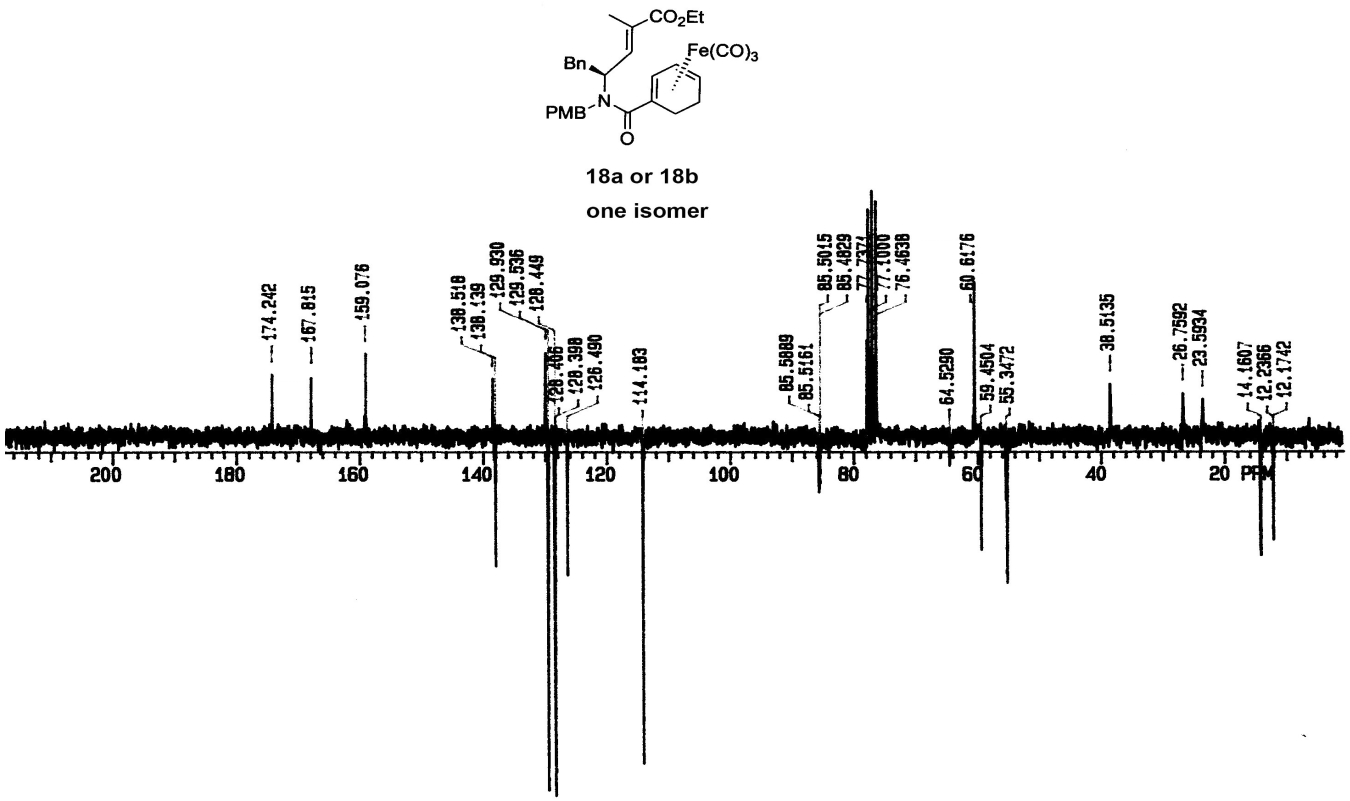
7.228
7.222
7.124
7.050
7.029
6.766
6.764
7.240
4.178
4.177
4.160
4.159
3.755
1.602
1.595
1.284
1.259
0.029
7
6
5
4
3
2
1
0
ppm

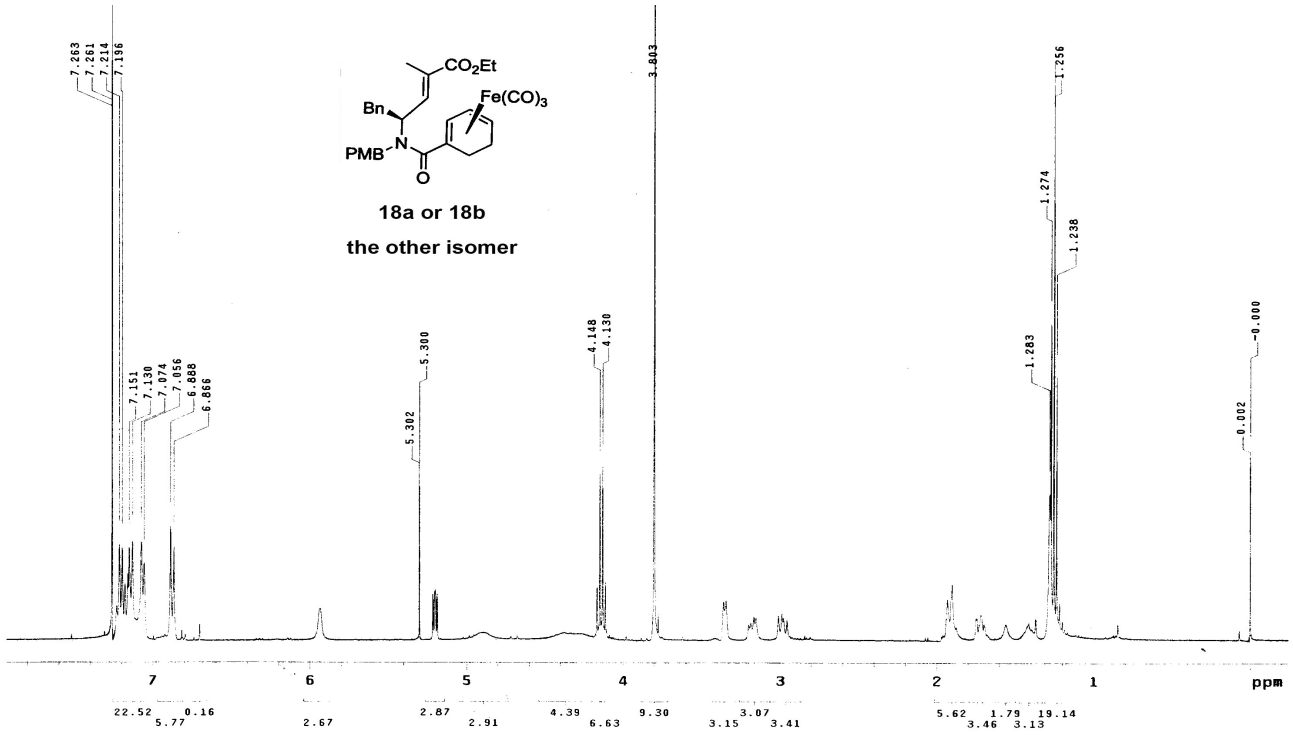

Bn
CO2Et
PMB
N
H
16
168.082
158.791
144.167
138.042
132.367
129.567
129.315
128.636
126.691
113.929
77.588
77.275
76.955
60.821
56.839
55.428
51.194
41.689
14.456
12.946
1.229
160
140
120
100
80
60
40
20
ppm

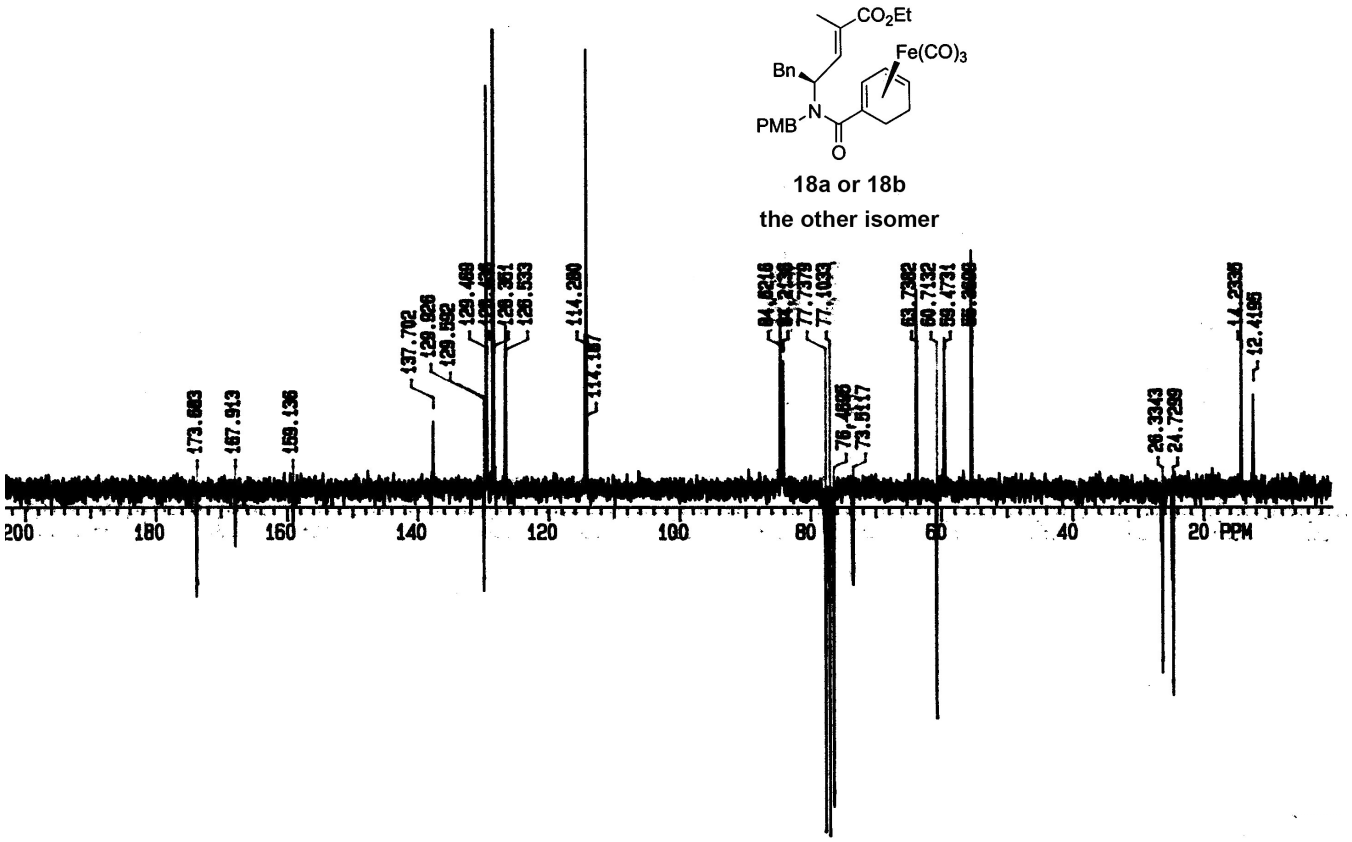

CO2Et
Bn
H
PMB
N
MTPA
17a
7.580
7.455
7.433
7.409
7.260
6.992
6.973
6.891
6.869
6.014
5.996
4.149
4.131
4.113
3.808
3.764
3.606
3.602
3.508
3.401
3.397
1.418
1.414
1.274
1.261
1.256
1.243
1.239
1.225
0.904
0.900
0.885
0.009
0.000
-0.008
8
7
6
5
4
3
2
1
ppm
18.65
7.61
7.59
1.75
3.17
3.34
2.67
1.19
5.88
7.01
2.58
3.23
4.63
1.63
1.22
2.16
2.05
2.80
12.29
8.53

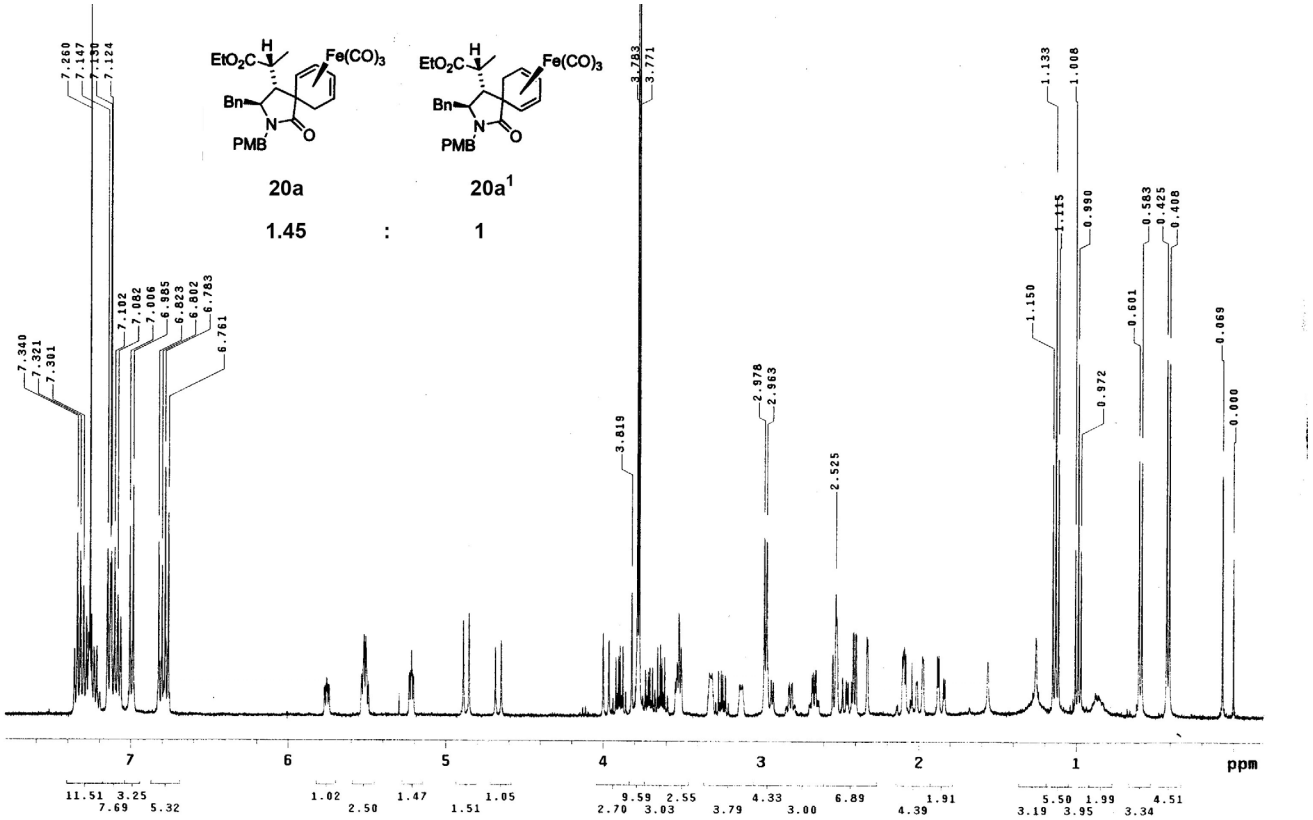

CO2Et
Bn
H
PMB
N
MTPA
17b
7.399
7.260
7.403
7.234
7.216
7.099
6.654
6.632
6.442
6.420
3.744
3.817
3.529
3.524
1.330
1.312
1.287
1.284
1.348
0.001
0.000
ppm

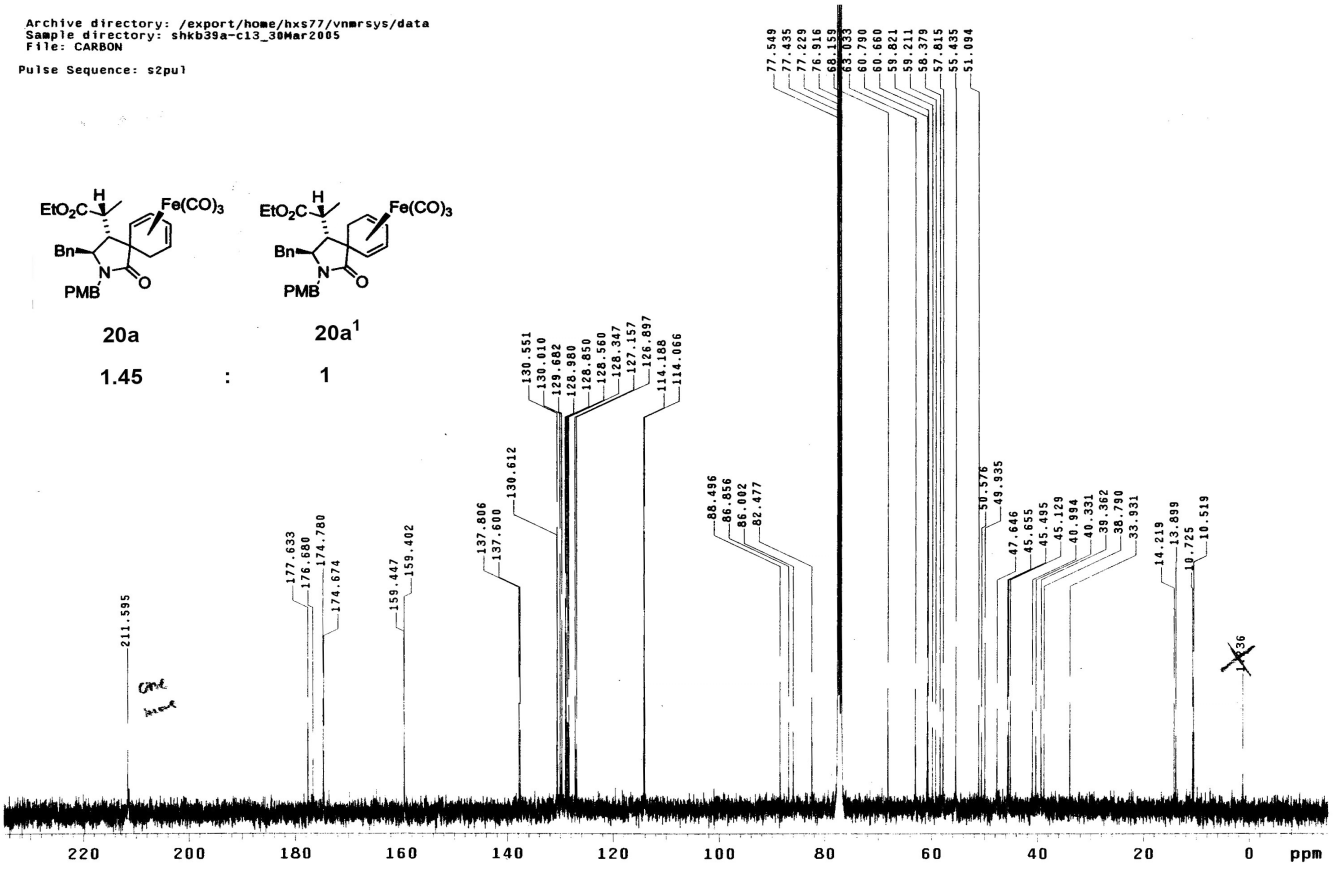

CO2Et
Fe(CO)3
Bn
PMB
N
O
18a or 18b
one isomer
3.802
7.262
7.217
7.191
7.139
7.066
7.061
7.046
7.043
6.947
6.926
6.815
6.810
6.793
4.713
4.673
4.136
4.119
4.103
4.086
1.374
1.370
1.235
1.217
1.199
ppm

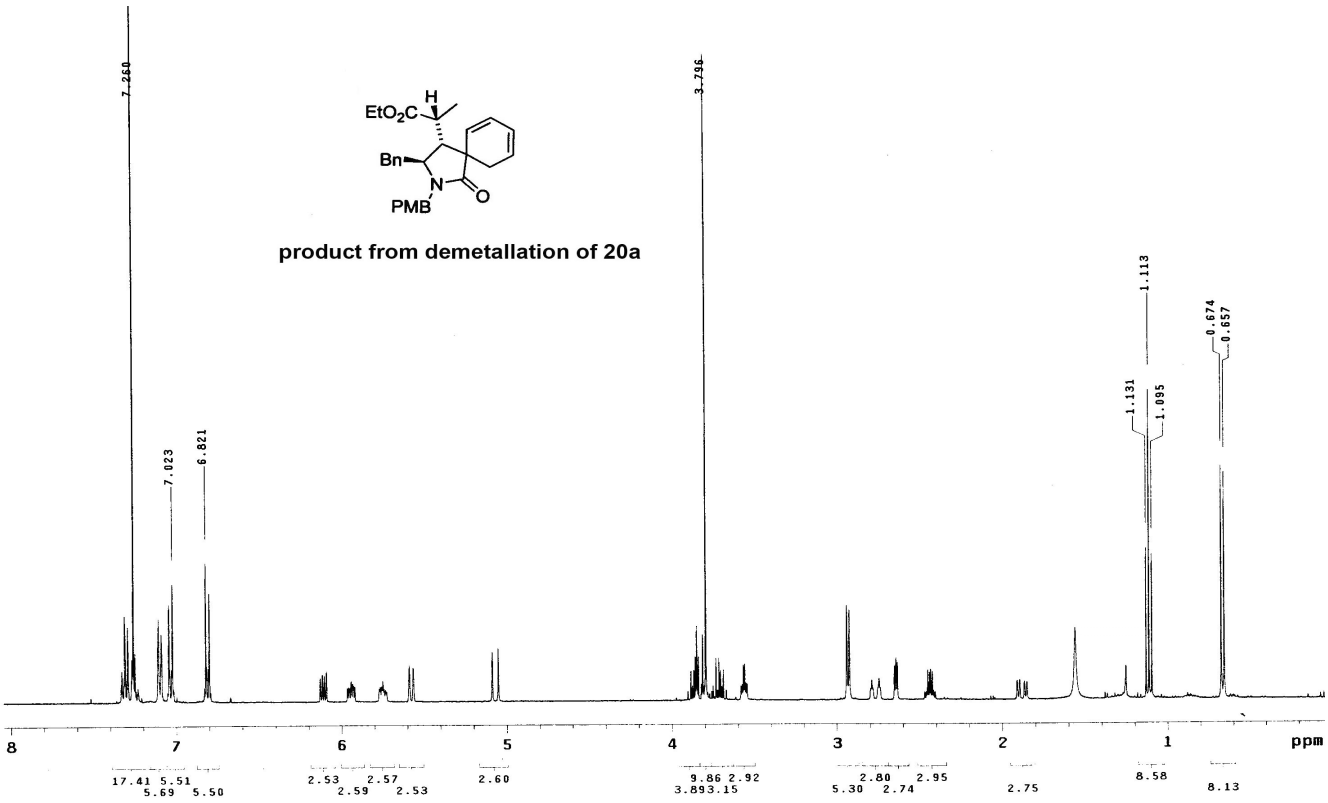

CO2Et
Fe(CO)3
Bn
N
PMB
O
18a or 18b
one isomer
174.242
167.815
159.076
138.518
138.139
129.930
129.536
128.449
128.406
128.398
126.490
114.183
85.5889
85.5161
85.5015
85.4829
77.7371
77.1000
76.4638
64.5290
60.6176
59.4504
55.3472
38.5135
26.7592
23.5934
14.1607
12.2366
12.1742
200
180
160
140
120
100
80
60
40
20 PPM


CO2Et
Fe(CO)3
Bn
N
PMB
O
18a or 18b
the other isomer
7.263
7.261
7.214
7.196
7.151
7.130
7.074
7.056
6.888
6.866
5.302
5.300
4.148
4.130
3.803
1.283
1.274
1.256
1.238
0.000
0.002
7
6
5
4
3
2
1
ppm
22.52
5.77
0.16
2.67
2.87
2.91
4.39
6.63
9.30
3.15
3.07
3.41
5.62
3.46
1.79
3.13
19.14

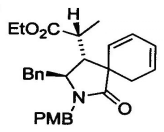

CO2Et
Fe(CO)3
Bn
PMB
N
O
18a or 18b
the other isomer
200
180
160
140
120
100
80
60
40
20 PPM


EtO2C
Fe(CO)3
Bn
PMB
20a
20a1
1.45 : 1
7
6
5
4
3
2
1
ppm

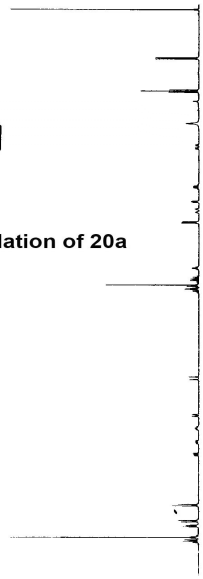

Archive directory: /export/home/hxs77/vnmrsys/data
Sample directory: shkb39a-c13_30Mar2005
File: CARBON
Pulse Sequence: s2pul
20a
20a1
1.45 : 1
ppm

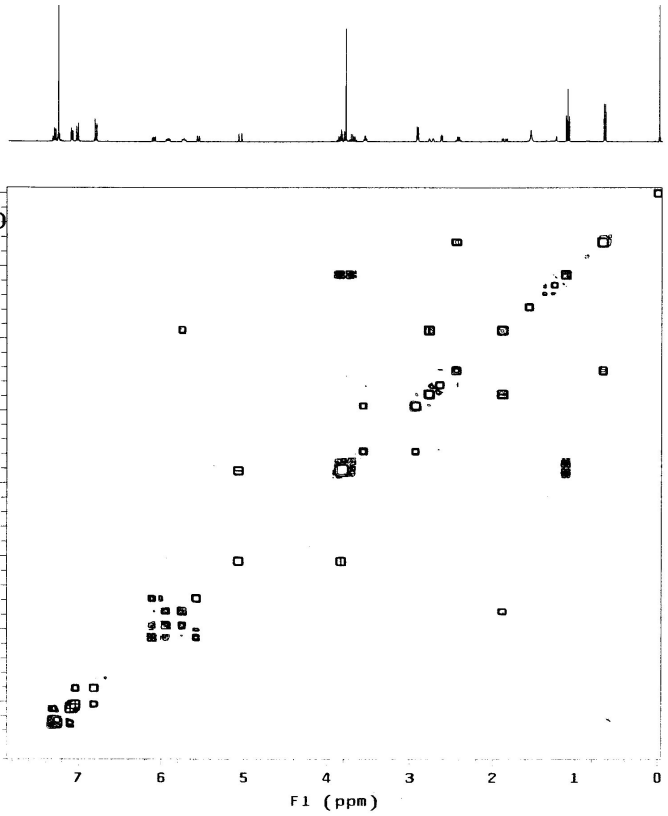

product from demetallation of 20a
ppm

```
Pulse Sequence: gCOSY
 Solvent: CDCl3
 Ambient temperature
INOVA-400  "chem400"

 Relax. delay 1.000 sec
 Acq. time 0.160 sec
 Width     6395.9 Hz
 2D Width 6395.9 Hz
 Single scan
 128 increments
OBSERVE    H1, 399.7467320 MHz
DATA PROCESSING
 Sq. sine bell 0.080 sec
F1 DATA PROCESSING
 Sq. sine bell 0.020 sec
FT size 2048 x 2048
Total time 2 min, 50 sec
```

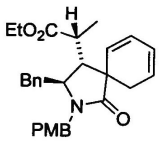


product from demetallation of 20a

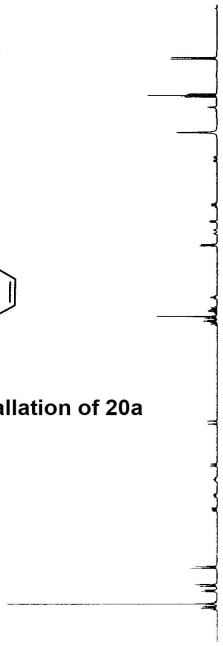


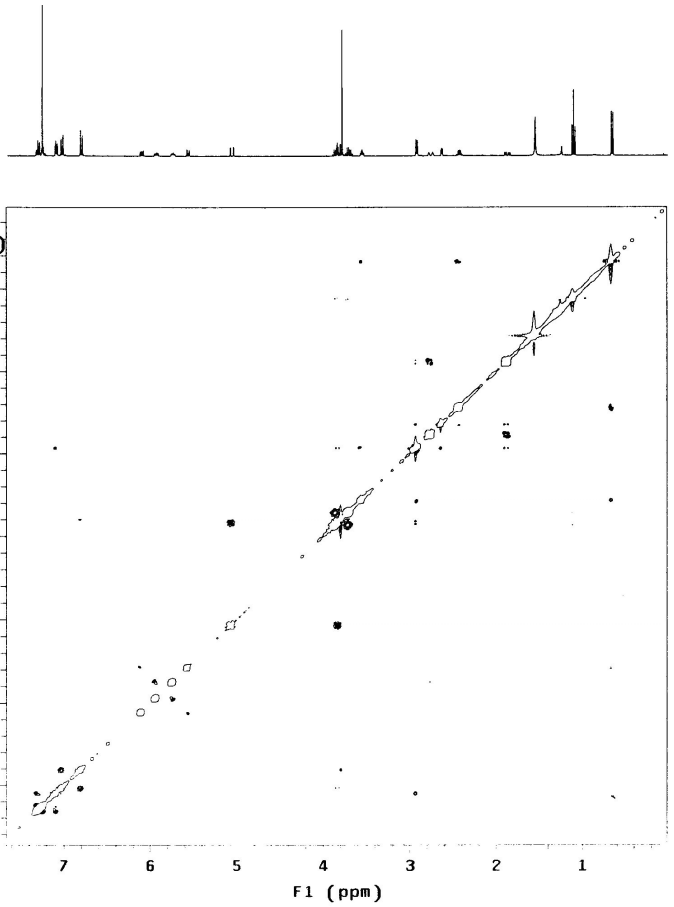


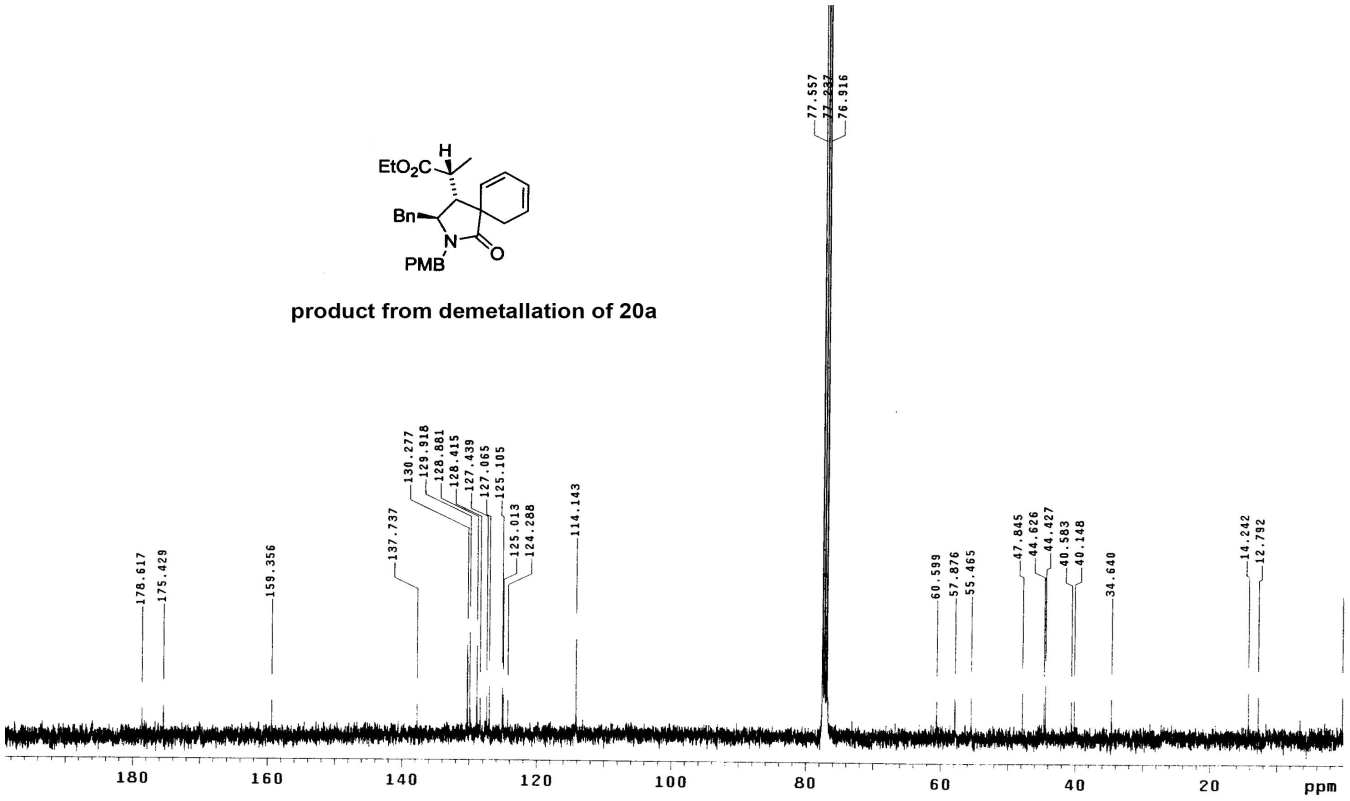

```
Pulse Sequence: NOESY
 Solvent: CDCl3
 Ambient temperature
INOVA-400  "chem400"

 Relax. delay 1.000 sec
 Mixing 0.200 sec
 Acq. time 0.160 sec
 Width     6395.9 Hz
 2D Width 6395.9 Hz
 16 repetitions
 2 x 512 increments
OBSERVE    H1, 399.7467320 MHz
DATA PROCESSING
 Gauss apodization 0.074 sec
F1 DATA PROCESSING
 Gauss apodization 0.074 sec
FT size 4096 x 4096
Total time 6 hr, 26 min, 47 sec
```

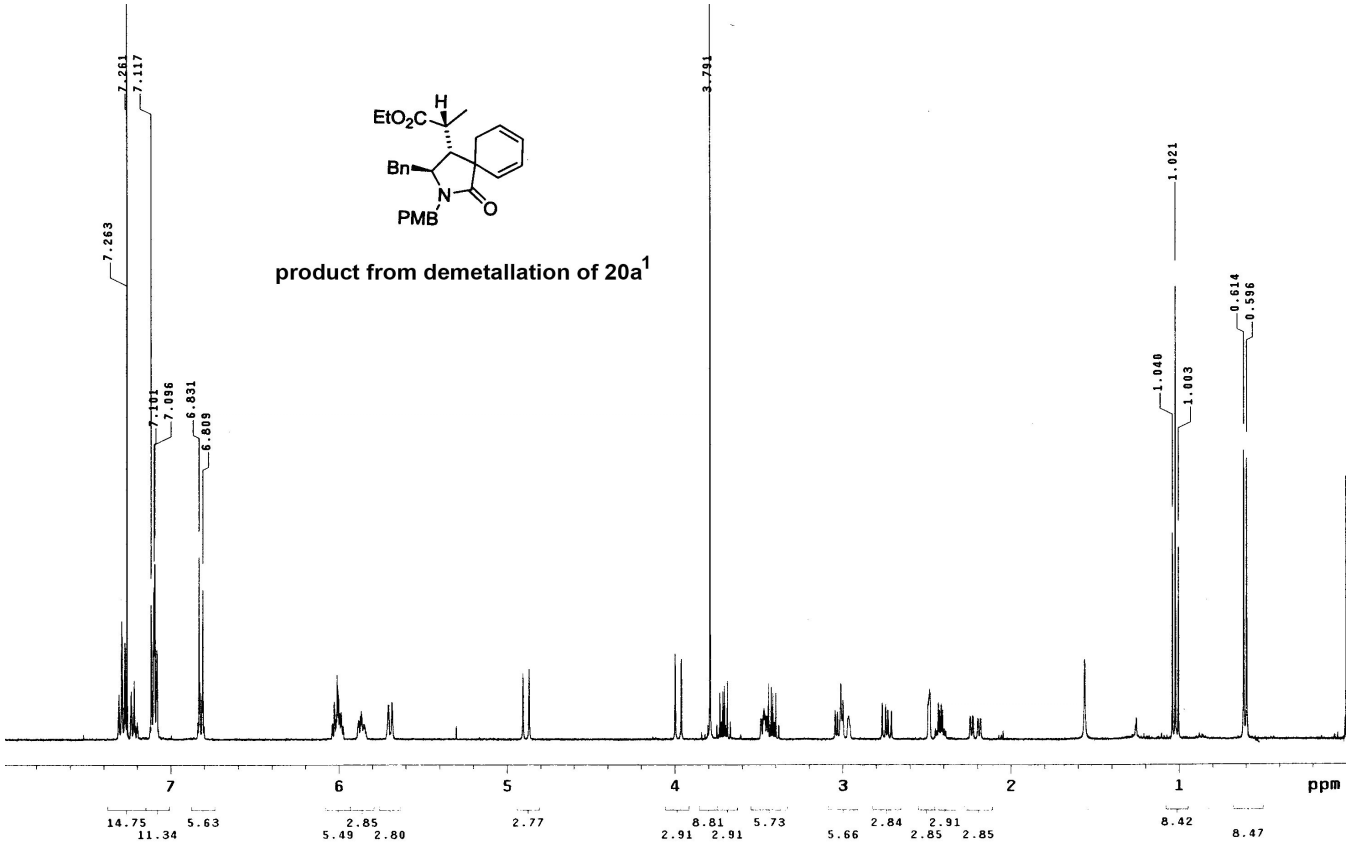


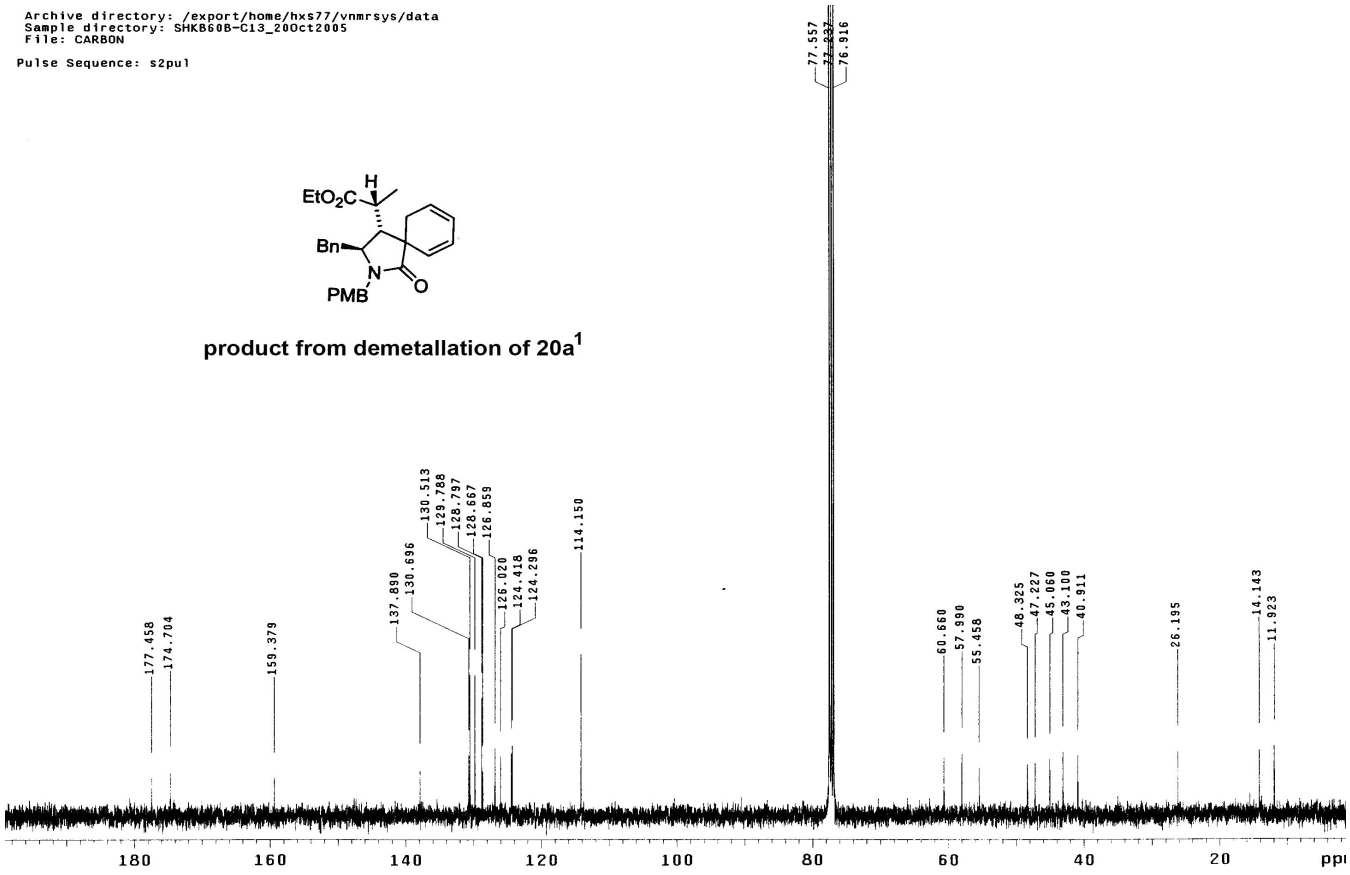
product from demetallation of 20a



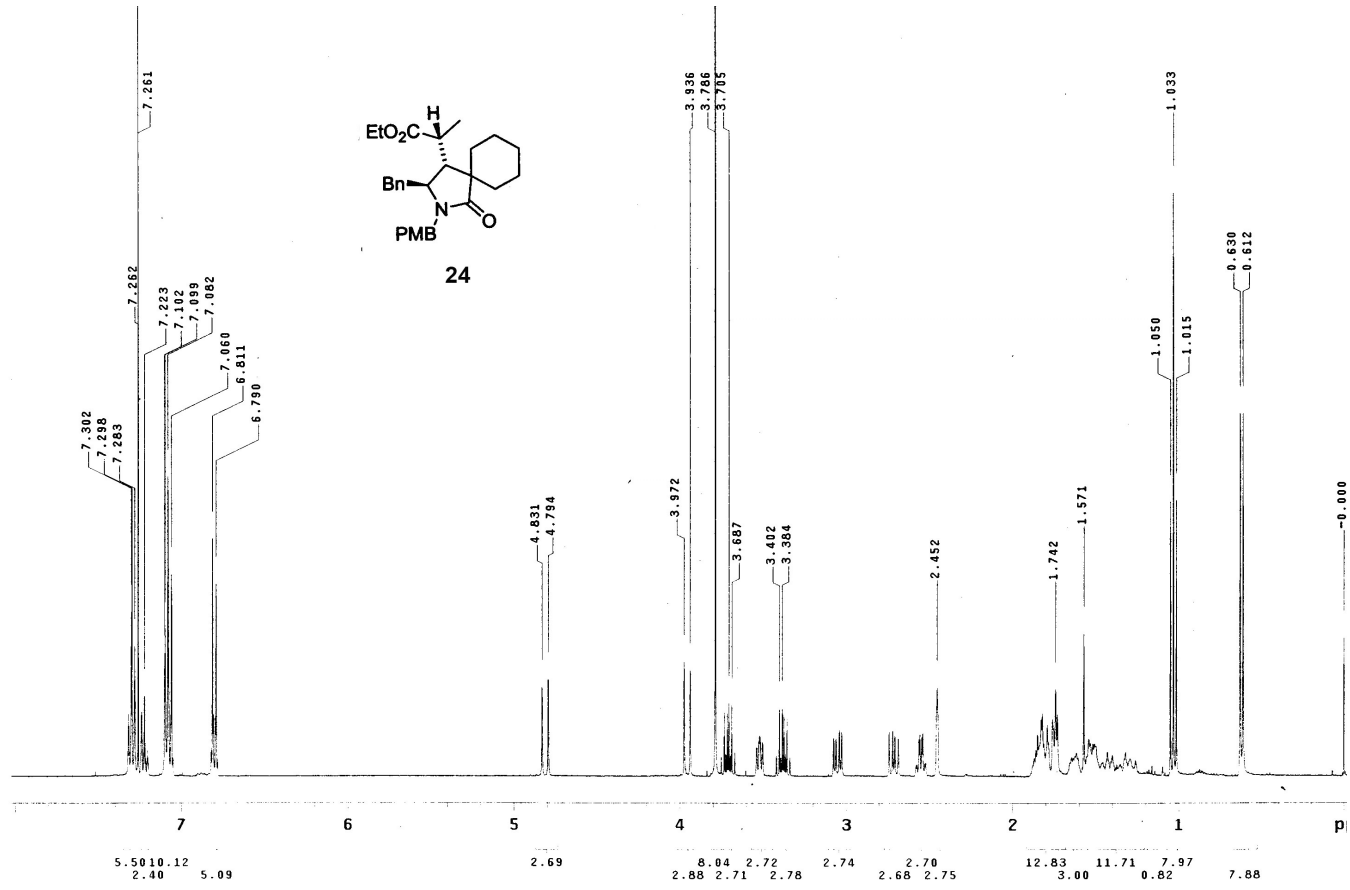


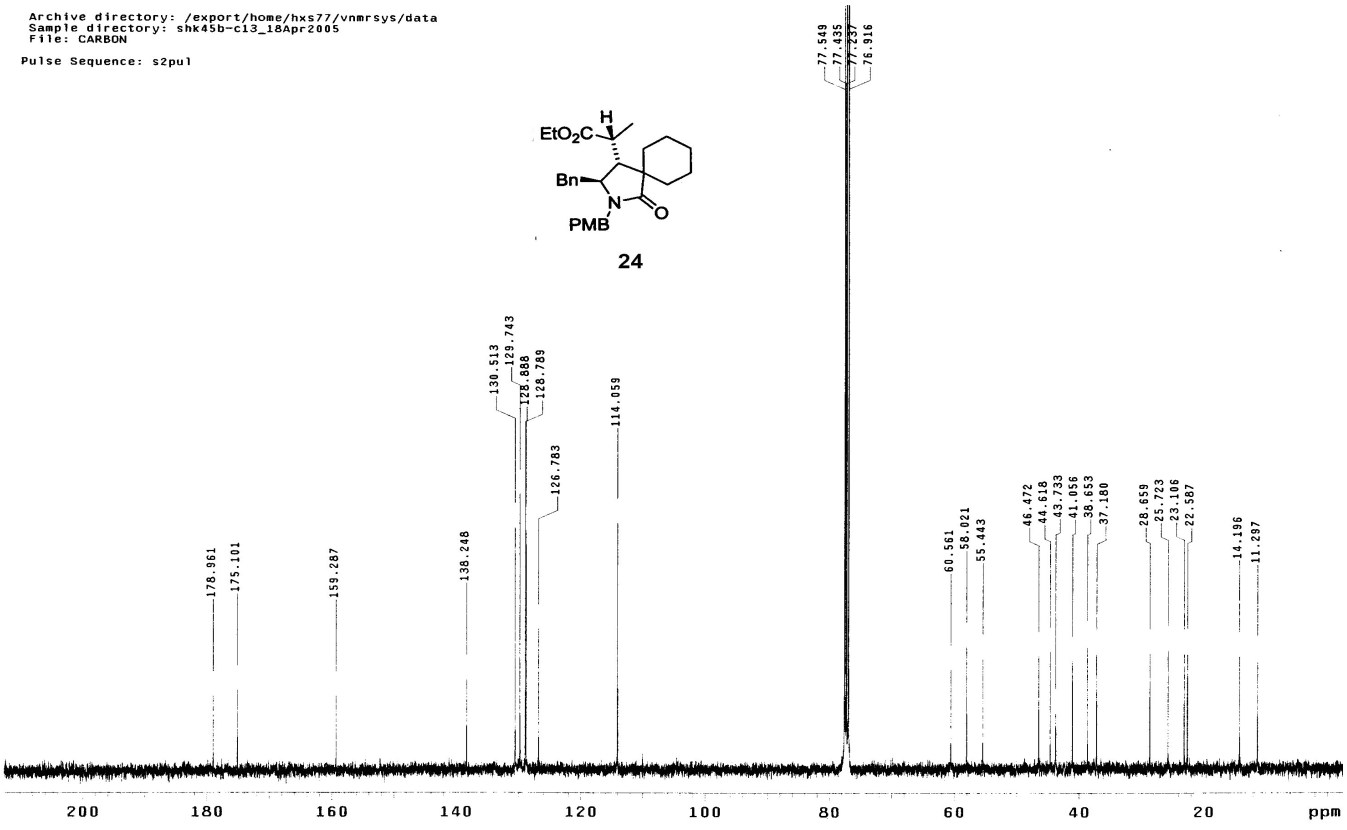

EtO2C
H
Bn
N
O
PMB
product from demetallation of 20a
77.557
77.232
76.916
178.617
175.429
159.356
137.737
130.277
129.918
128.881
128.415
127.439
127.065
125.105
125.013
124.288
114.143
60.599
57.876
55.465
47.845
44.626
44.427
40.583
40.148
34.640
14.242
12.792
180
160
140
120
100
80
60
40
20
ppm

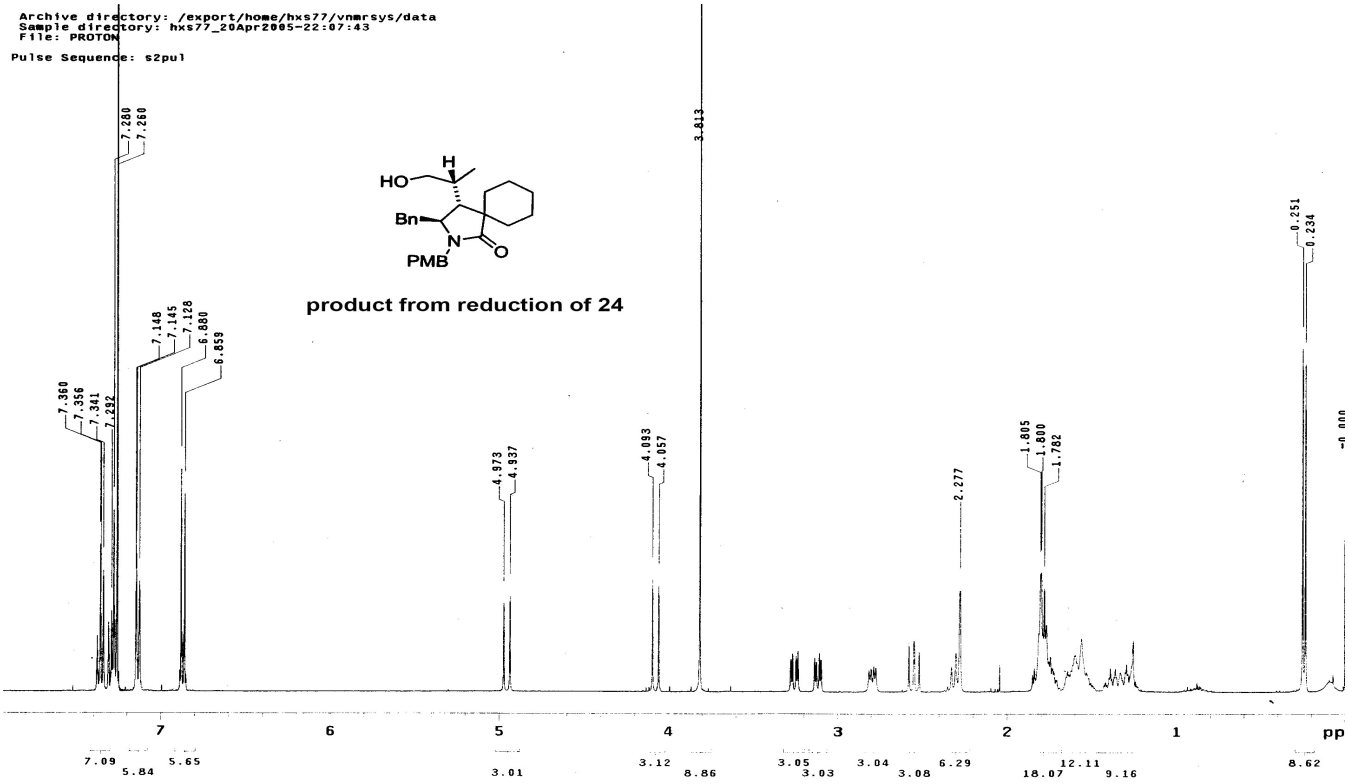

EtO2C
H
Bn
N
O
PMB
product from demetallation of 20a[1]
7.263
7.261
7.117
7.101
7.096
6.831
6.809
3.791
1.021
1.040
1.003
0.614
0.596
7
6
5
4
3
2
1
ppm
14.75
11.34
5.63
2.85
5.49
2.80
2.77
8.81
2.91
2.91
5.73
5.66
2.84
2.91
2.85
2.85
8.42
8.47

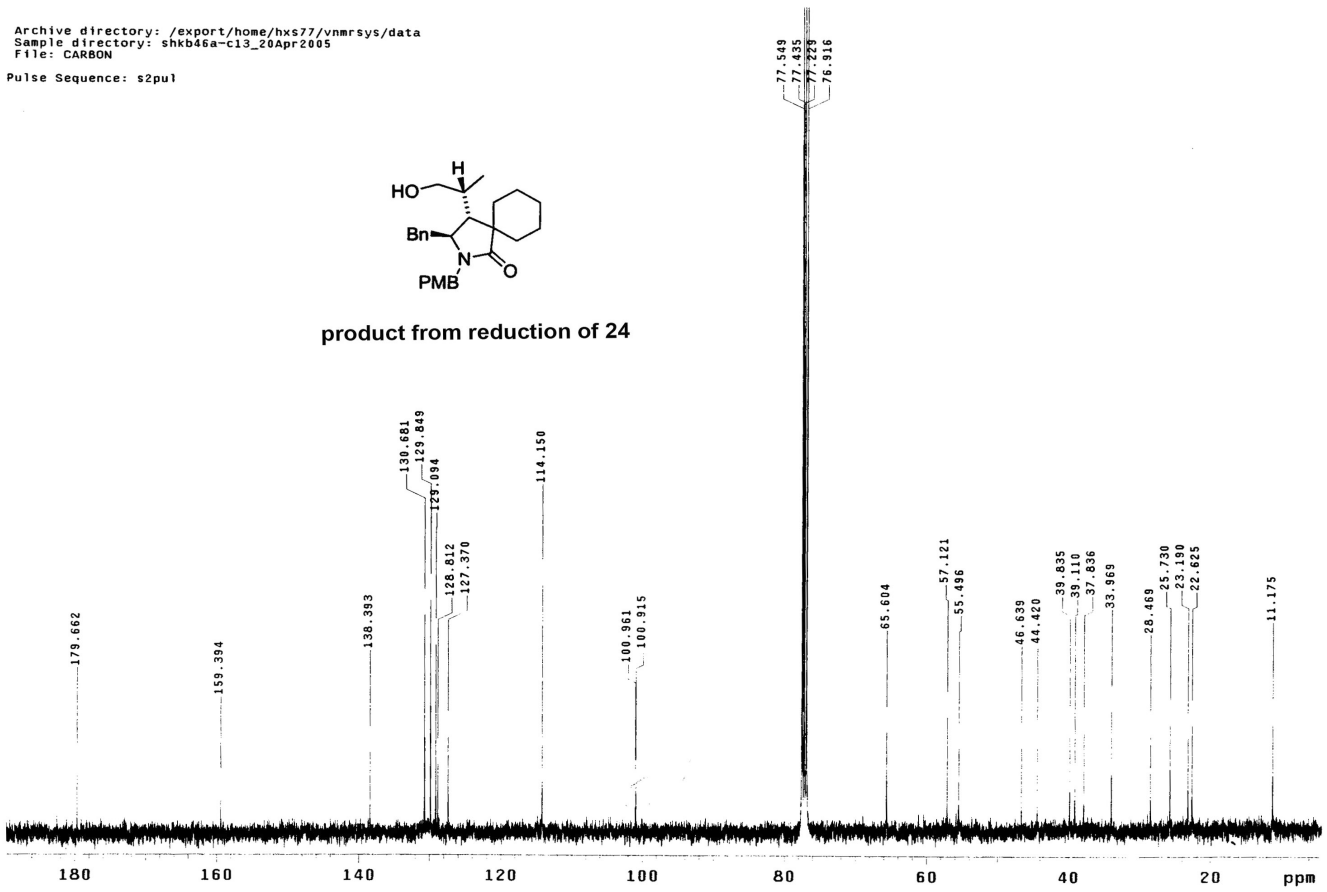


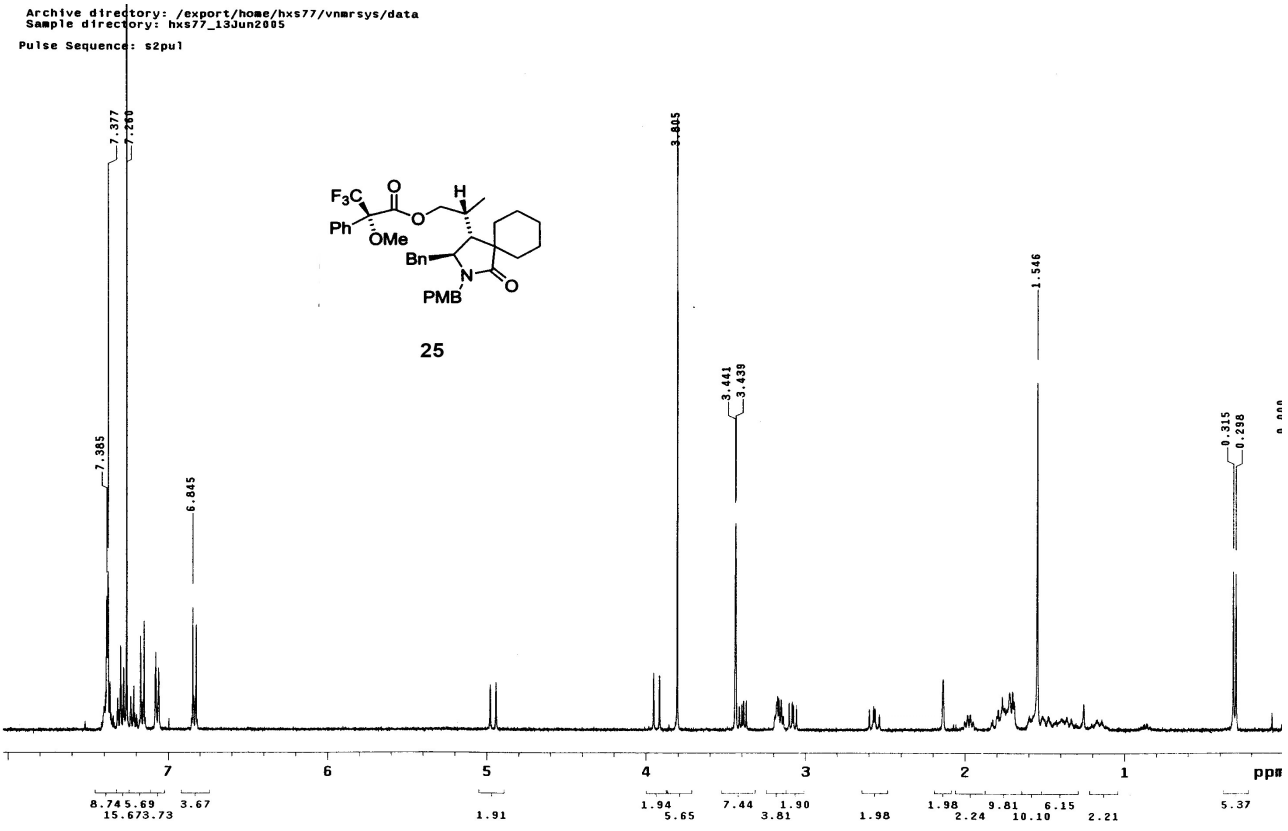
product from demetallation of 20a[1]

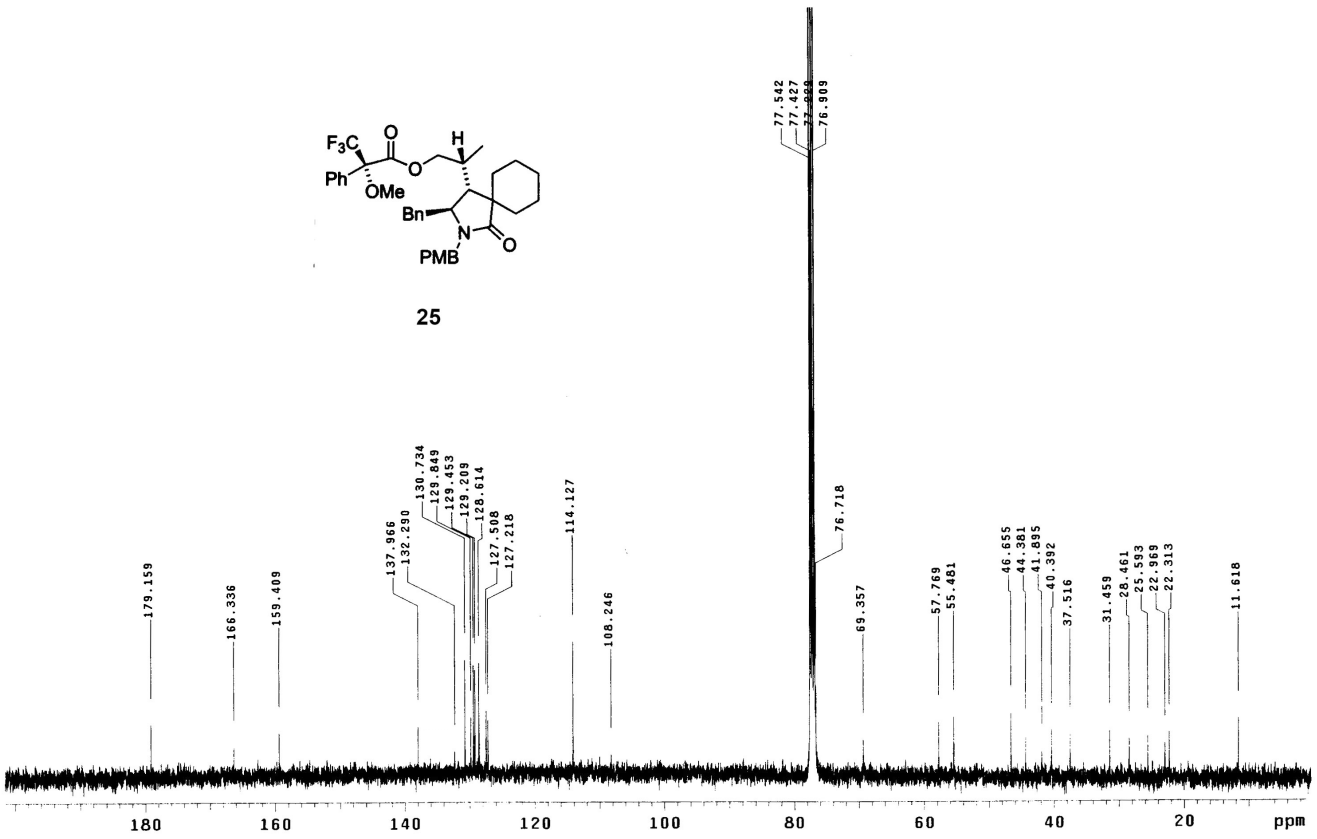



Archive directory: /export/home/hxs77/vnmrsys/data
Sample directory: shk45b-c13_18Apr2005
File: CARBON
Pulse Sequence: s2pul
EtO2C
H
Bn
N
O
PMB
24
77.549
77.435
77.237
76.916
130.513
129.743
128.888
128.789
126.783
114.059
178.961
175.101
159.287
138.248
60.561
58.021
55.443
46.472
44.618
43.733
41.056
38.653
37.180
28.659
25.723
23.106
22.587
14.196
11.297
200
180
160
140
120
100
80
60
40
20
ppm

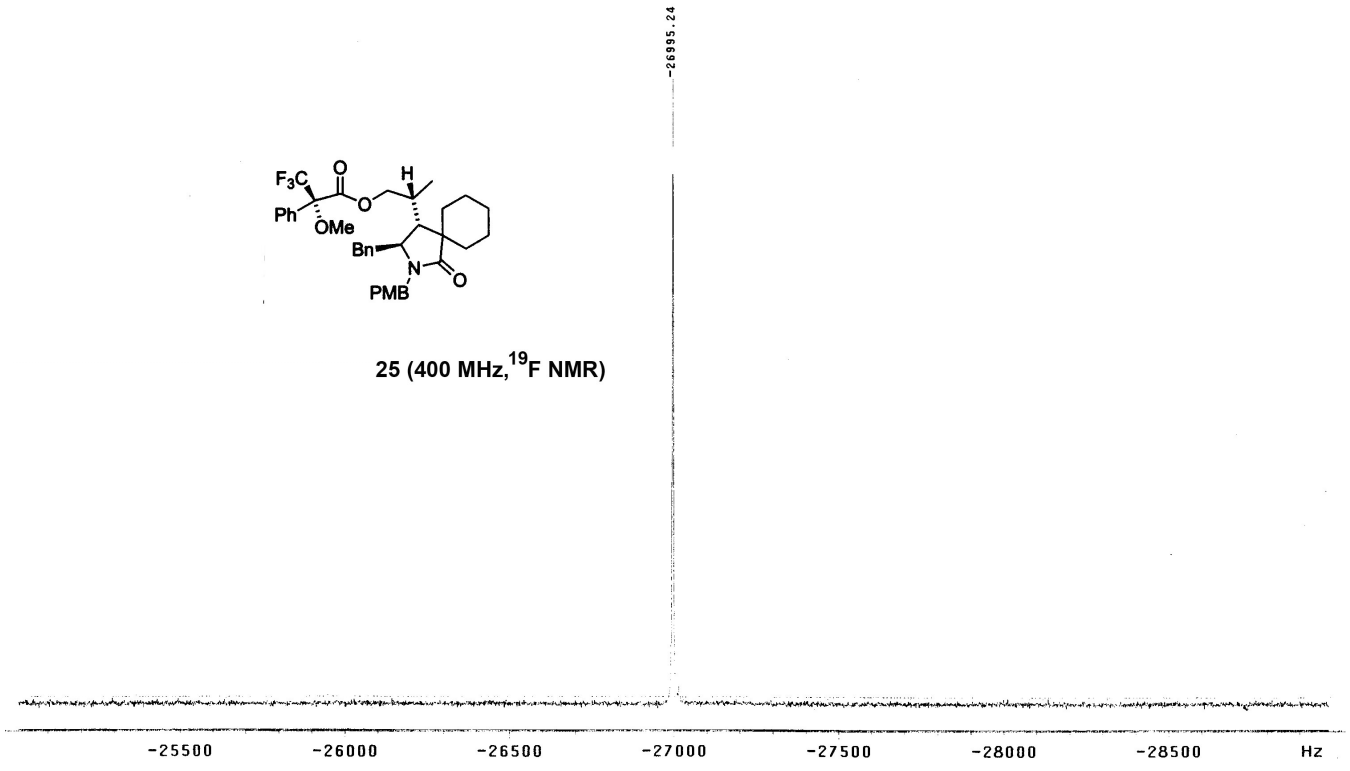

Archive directory: /export/home/hxs77/vnmrsys/data
Sample directory: hxs77_20Apr2005-22:07:43
File: PROTON
Pulse Sequence: s2pul
HO
H
Bn
N
O
PMB
product from reduction of 24
7.280
7.260
7.360
7.356
7.341
7.292
7.148
7.145
7.128
6.880
6.859
4.973
4.937
4.093
4.057
3.813
2.277
1.805
1.800
1.782
0.251
0.234
7
6
5
4
3
2
1
pp
7.09
5.84
5.65
3.01
3.12
8.86
3.05
3.03
3.04
3.08
6.29
18.07
12.11
9.16
8.62


Archive directory: /export/home/hxs77/vnmrsys/data
Sample directory: shkb46a-c13_20Apr2005
File: CARBON
Pulse Sequence: s2pul
HO
H
Bn
N
O
PMB
product from reduction of 24
77.549
77.435
77.229
76.916
130.681
129.849
129.094
128.812
127.370
114.150
179.662
159.394
138.393
100.961
100.915
65.604
57.121
55.496
46.639
44.420
39.835
39.110
37.836
33.969
28.469
25.730
23.190
22.625
11.175
180
160
140
120
100
80
60
40
20
ppm

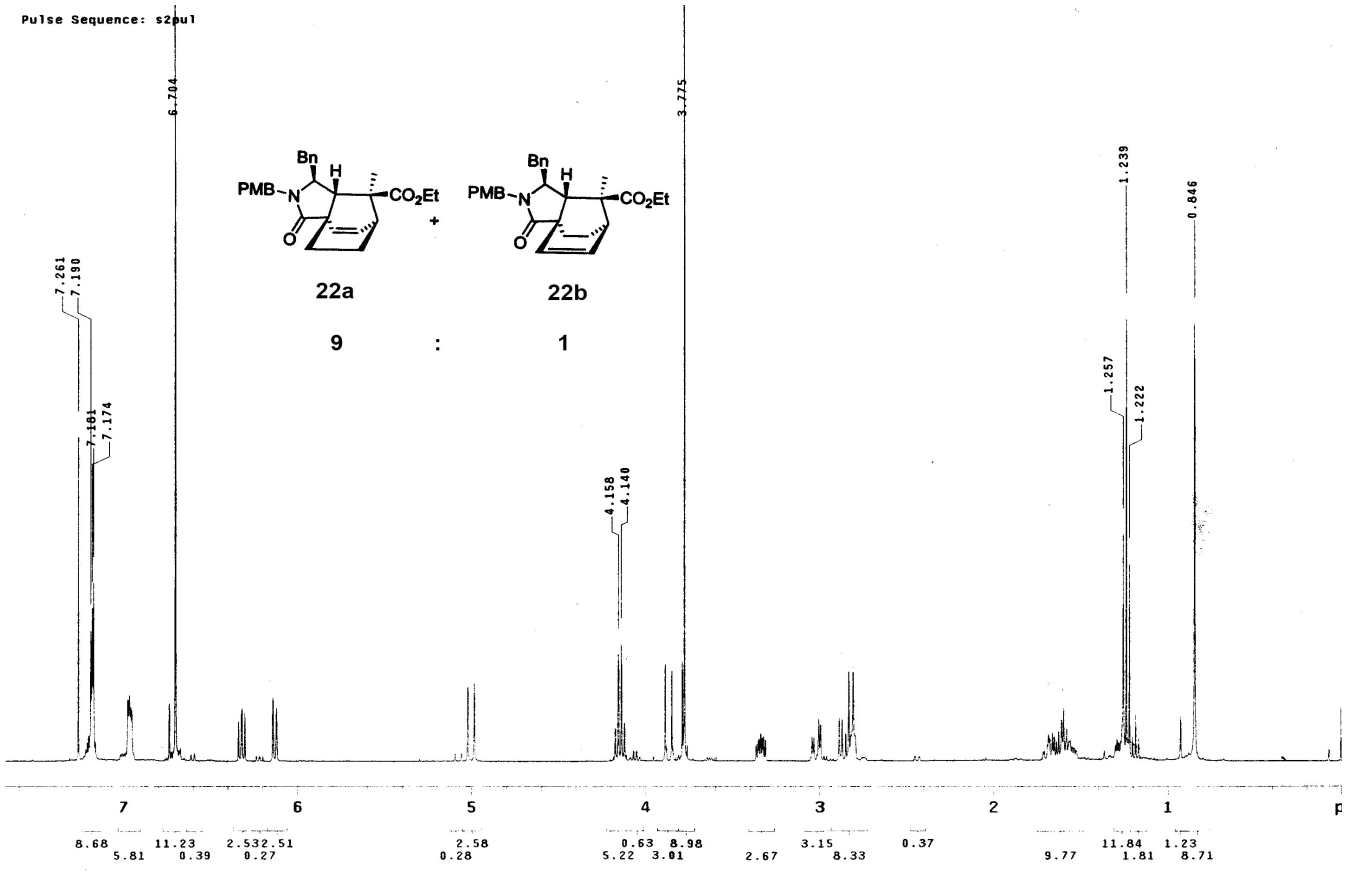

Archive directory: /export/home/hxs77/vnmrsys/data
Sample directory: hxs77_13Jun2005
Pulse Sequence: s2pul
F3C
O
O
H
Ph
OMe
Bn
N
O
PMB
25
7.377
7.260
7.385
6.845
3.805
3.441
3.439
1.546
0.315
0.298
7
6
5
4
3
2
1
ppm
8.74
5.69
15.67
3.73
3.67
1.91
1.94
5.65
7.44
1.90
3.81
1.98
1.98
2.24
9.81
10.10
6.15
2.21
5.37

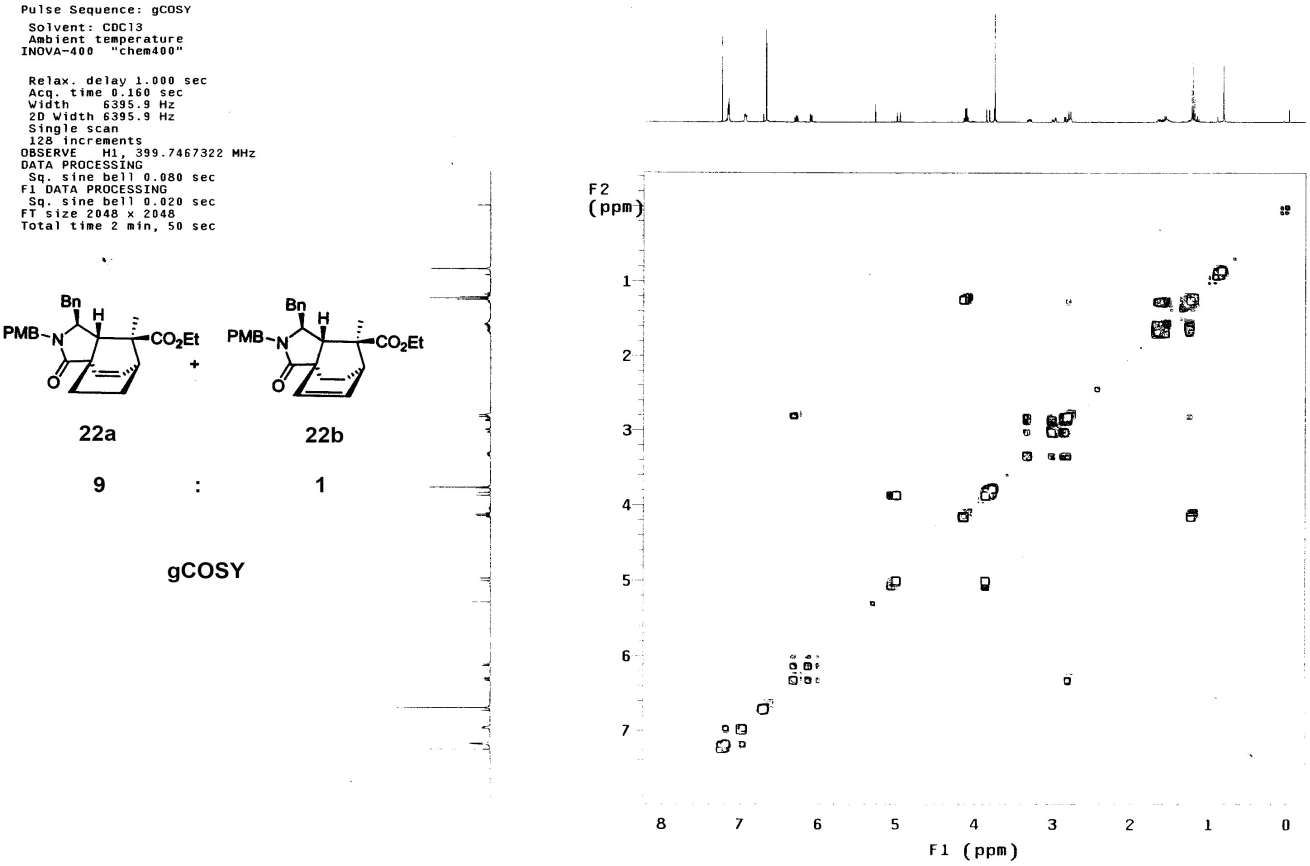


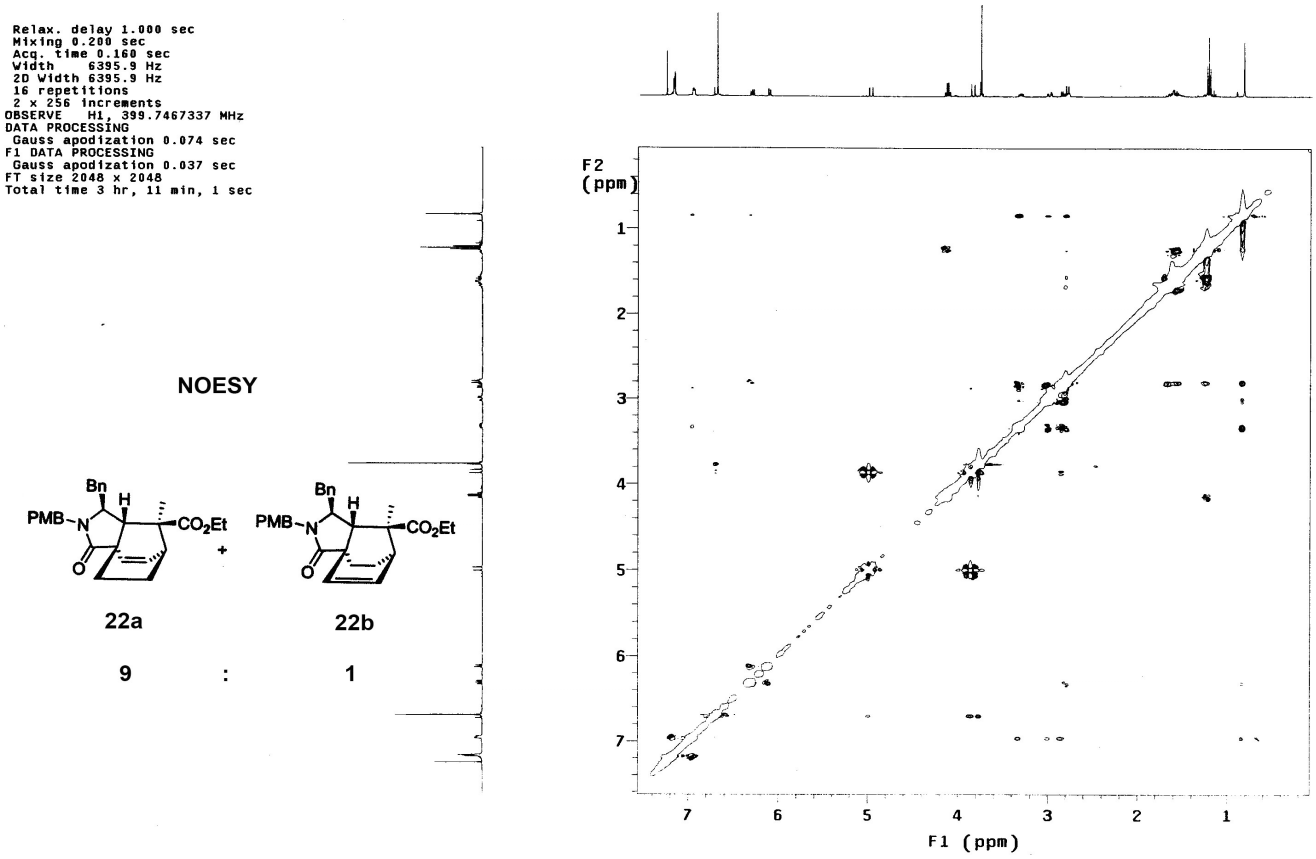
25

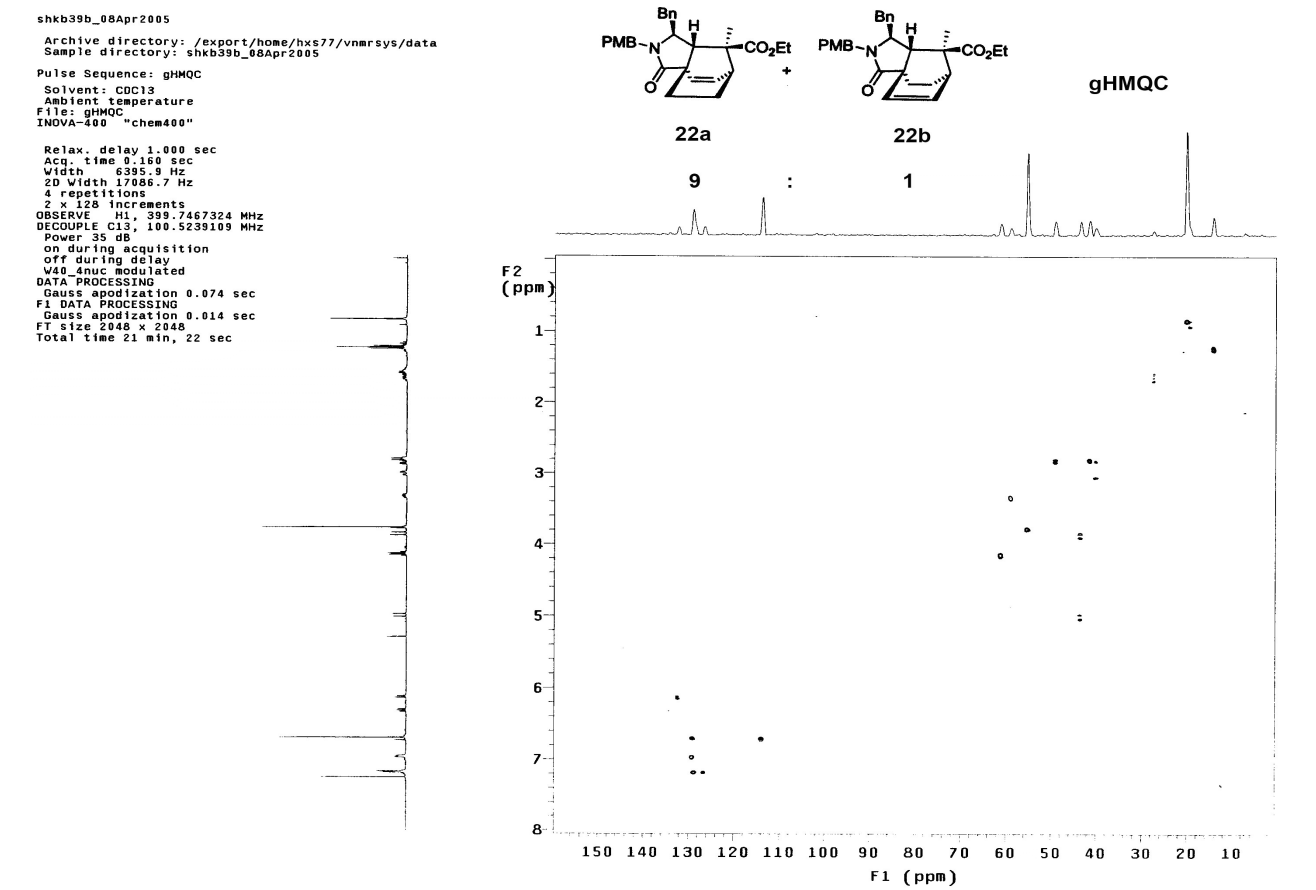


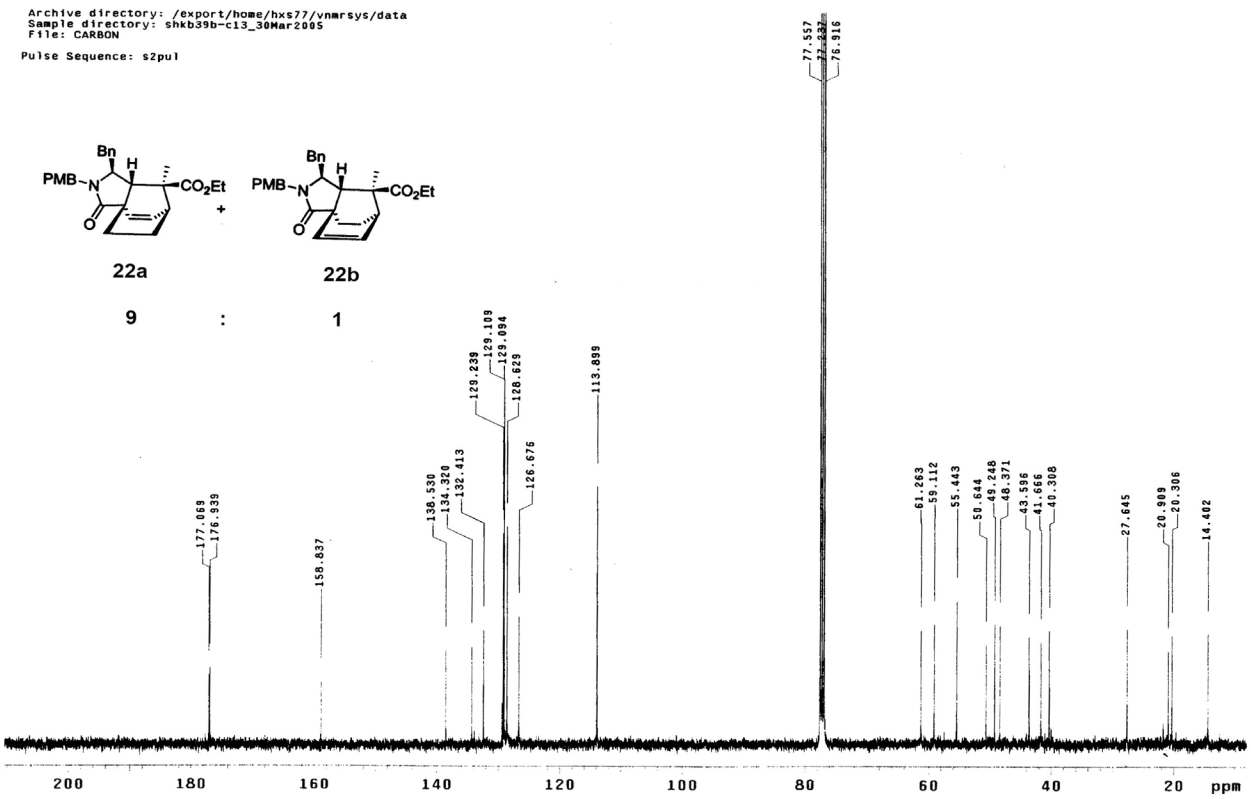
25 (400 MHz, ^{19}F NMR)

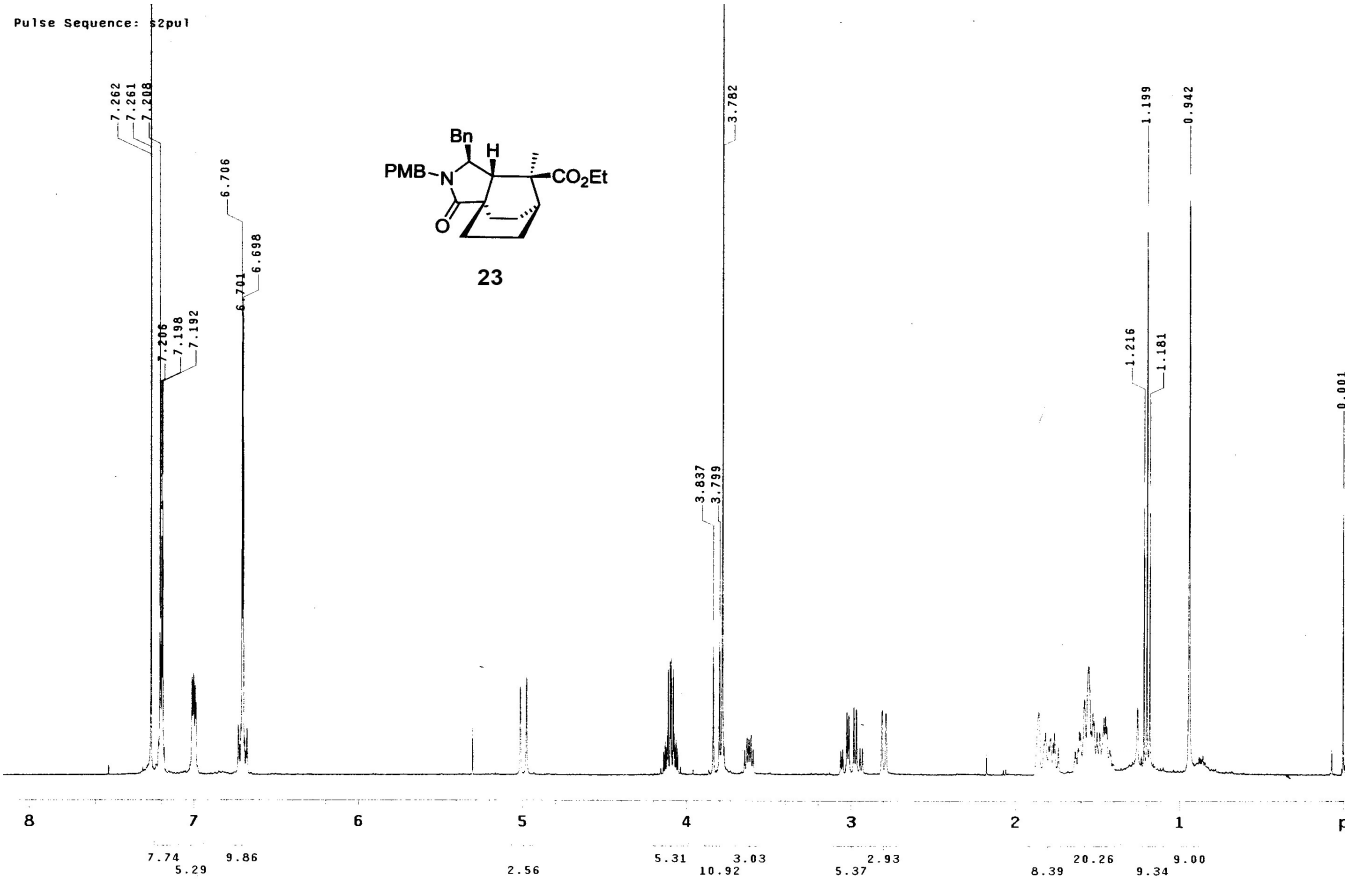

Pulse Sequence: s2pul
6.704
3.775
7.261
7.190
7.181
7.174
4.158
4.140
1.239
0.846
1.257
1.222
22a
22b
9 : 1


Pulse Sequence: gCOSY
Solvent: CDCl3
Ambient temperature
INOVA-400 "chem400"
Relax. delay 1.000 sec
Acq. time 0.160 sec
Width 6395.9 Hz
2D Width 6395.9 Hz
Single scan
128 increments
OBSERVE H1, 399.7467322 MHz
DATA PROCESSING
Sq. sine bell 0.080 sec
F1 DATA PROCESSING
Sq. sine bell 0.020 sec
FT size 2048 x 2048
Total time 2 min, 50 sec
22a
22b
9 : 1
gCOSY
F2 (ppm)
F1 (ppm)

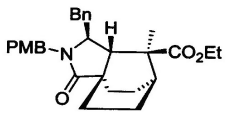

Relax. delay 1.000 sec
Mixing 0.200 sec
Acq. time 0.160 sec
Width 6395.9 Hz
2D Width 6395.9 Hz
16 repetitions
2 x 256 increments
OBSERVE H1, 399.7467337 MHz
DATA PROCESSING
Gauss apodization 0.074 sec
F1 DATA PROCESSING
Gauss apodization 0.037 sec
FT size 2048 x 2048
Total time 3 hr, 11 min, 1 sec
NOESY
Bn
H
PMB
N
O
CO2Et
+
22a
22b
9 : 1
F2 (ppm)
F1 (ppm)


shkb39b_08Apr2005
Archive directory: /export/home/hxs77/vnmrsys/data
Sample directory: shkb39b_08Apr2005
Pulse Sequence: gHMQC
Solvent: CDCl3
Ambient temperature
File: gHMQC
INOVA-400 "chem400"
Relax. delay 1.000 sec
Acq. time 0.160 sec
Width 6395.9 Hz
2D Width 17086.7 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 399.7467324 MHz
DECOUPLE C13, 100.5239109 MHz
Power 35 dB
on during acquisition
off during delay
W40_4nuc modulated
DATA PROCESSING
Gauss apodization 0.074 sec
F1 DATA PROCESSING
Gauss apodization 0.014 sec
FT size 2048 x 2048
Total time 21 min, 22 sec
Bn
H
PMB
N
O
CO2Et
+
22a
22b
9 : 1
gHMQC
F2 (ppm)
F1 (ppm)


Archive directory: /export/home/hxs77/vnmrsys/data
Sample directory: shkb39b-c13_30Mar2005
File: CARBON
Pulse Sequence: s2pul
22a
22b
9 : 1
77.557
77.232
76.916
177.069
176.939
158.837
138.530
134.320
132.413
129.239
129.109
129.094
128.629
126.676
113.899
61.263
59.112
55.443
50.644
49.248
48.371
43.596
41.666
40.308
27.645
20.909
20.306
14.402
200
180
160
140
120
100
80
60
40
20
ppm

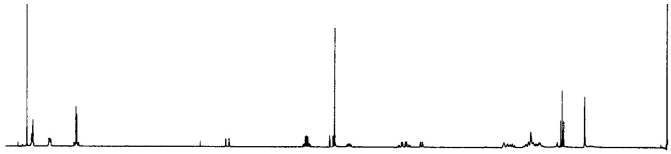

Pulse Sequence: s2pul
23
7.262
7.261
7.208
7.206
7.198
7.192
6.706
6.701
6.698
3.782
3.837
3.799
1.216
1.199
1.181
0.942
0.001
8
7
6
5
4
3
2
1
7.74
5.29
9.86
2.56
5.31
10.92
3.03
5.37
2.93
8.39
20.26
9.34
9.00

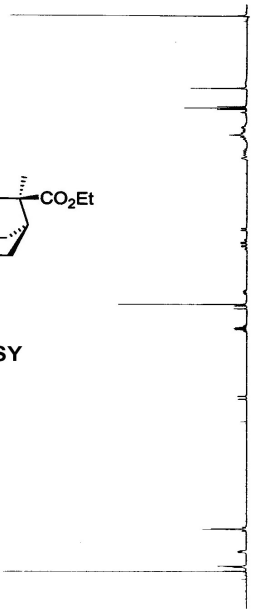
```
Pulse Sequence: gCOSY
 Solvent: CDCl3
 Ambient temperature
INOVA-400  "chem400"

 Relax. delay 1.000 sec
 Acq. time 0.160 sec
 Width    6395.9 Hz
 2D Width 6395.9 Hz
 Single scan
 128 increments
OBSERVE    H1, 399.7467324 MHz
DATA PROCESSING
 Sq. sine bell 0.080 sec
F1 DATA PROCESSING
 Sq. sine bell 0.020 sec
FT size 2048 x 2048
Total time 2 min, 50 sec
```

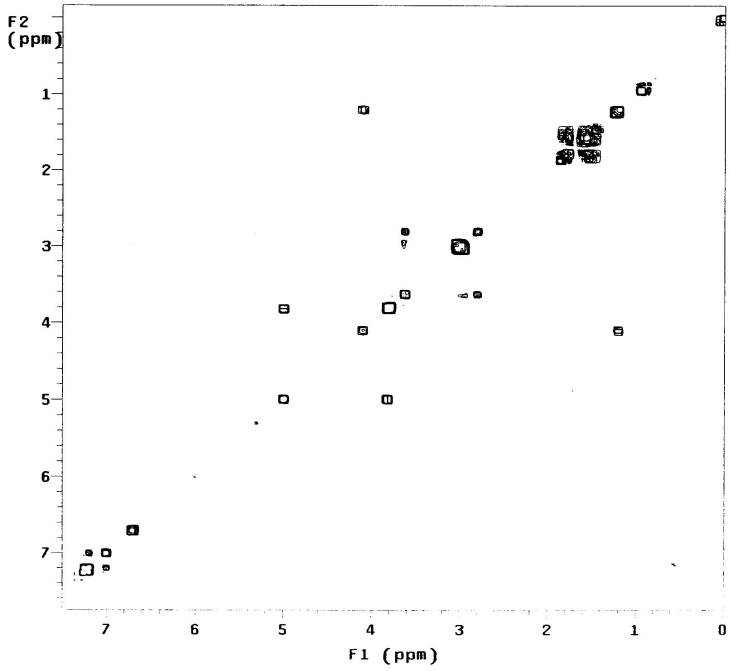


23

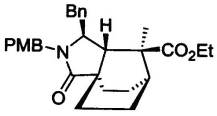
gCOSY





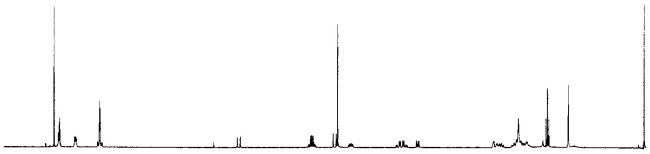


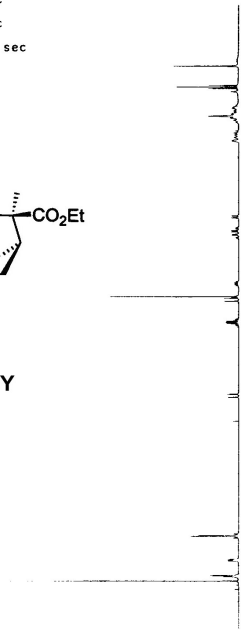

```
Pulse Sequence: NOESY
 Solvent: CDCl3
 Ambient temperature
INOVA-400  "chem400"

 Relax. delay 1.000 sec
 Mixing 0.200 sec
 Acq. time 0.160 sec
 Width    6395.9 Hz
 2D Width 6395.9 Hz
 16 repetitions
 2 x 512 increments
OBSERVE    H1, 399.7467314 MHz
DATA PROCESSING
 Gauss apodization 0.074 sec
F1 DATA PROCESSING
 Gauss apodization 0.074 sec
FT size 4096 x 4096
Total time 6 hr, 26 min, 47 sec
```

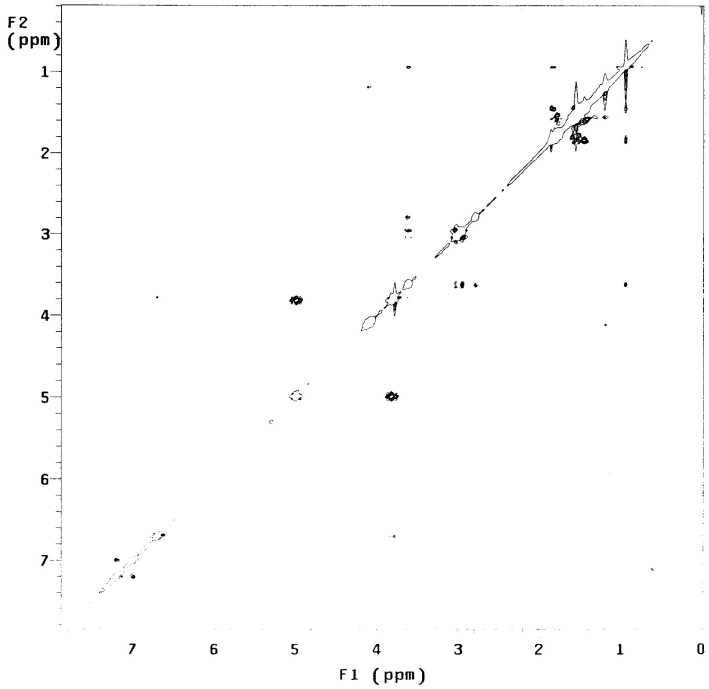


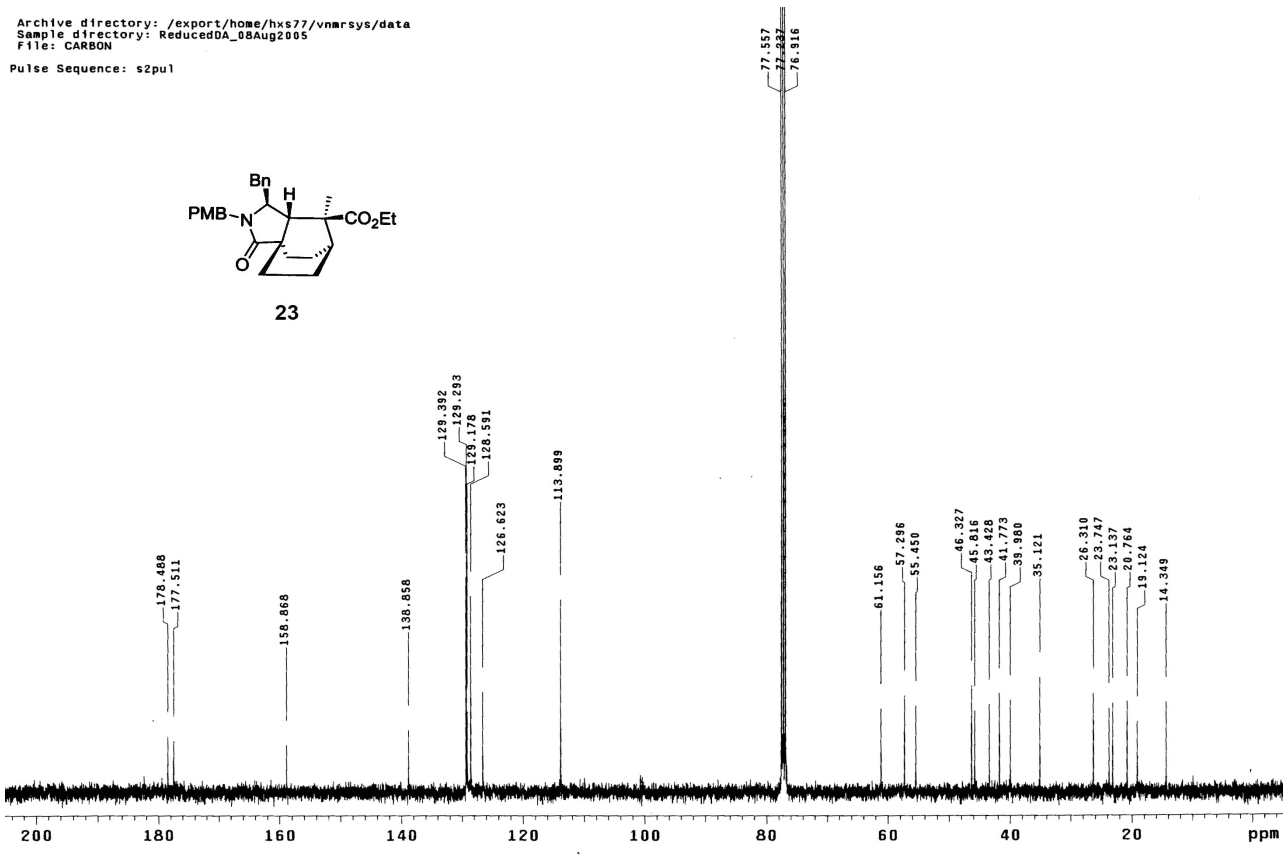
23

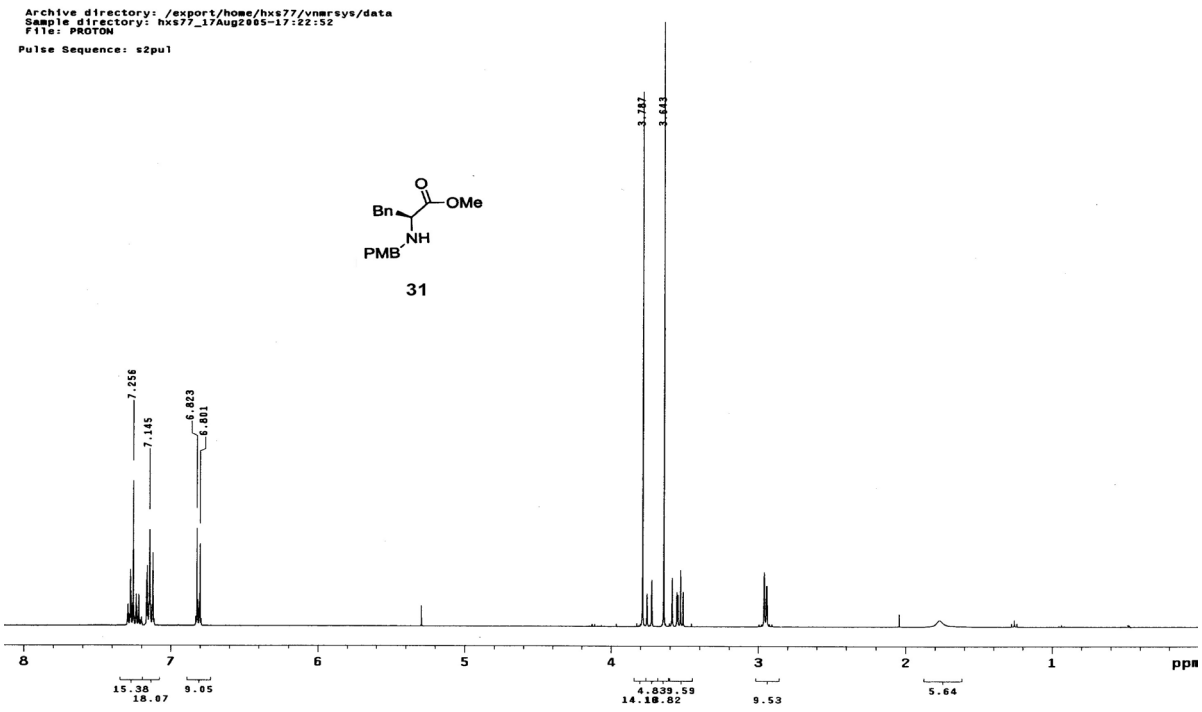
NOESY

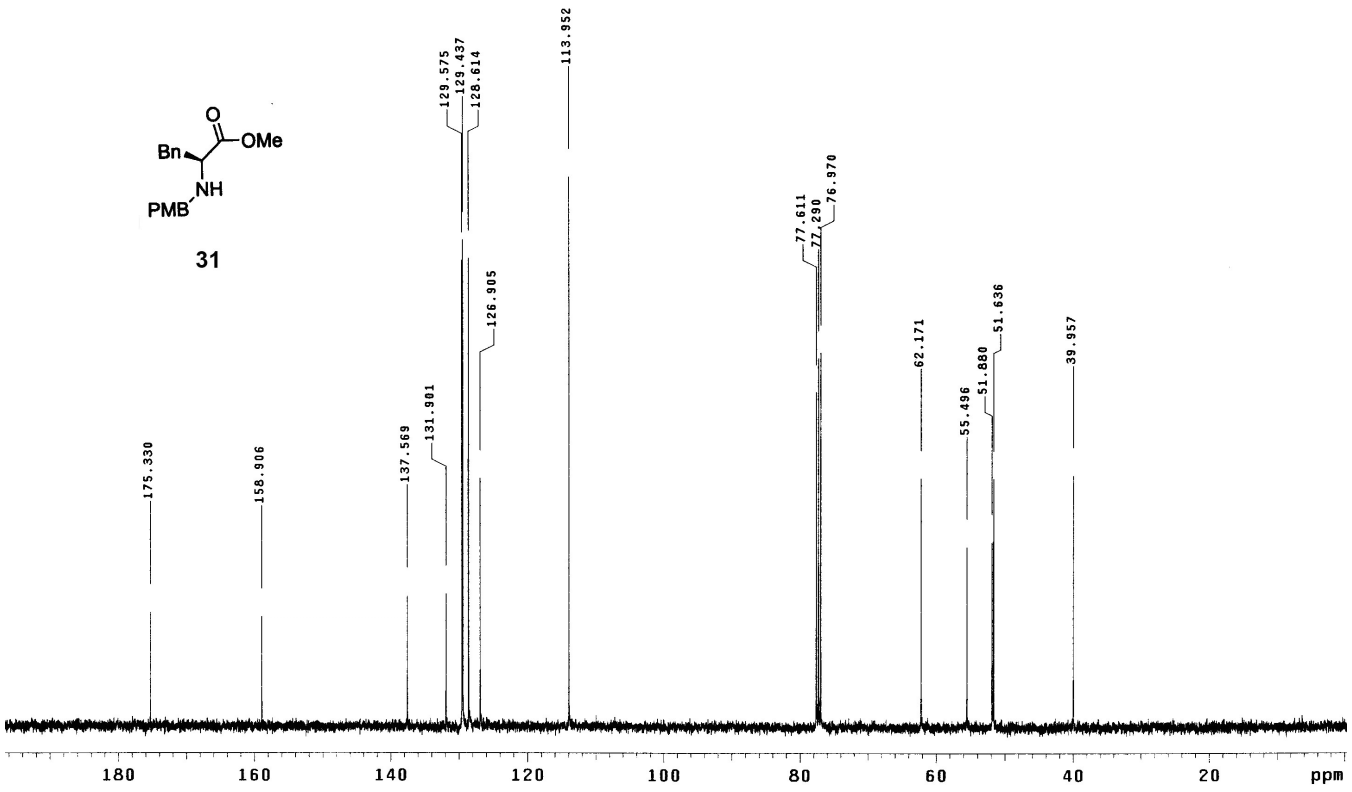


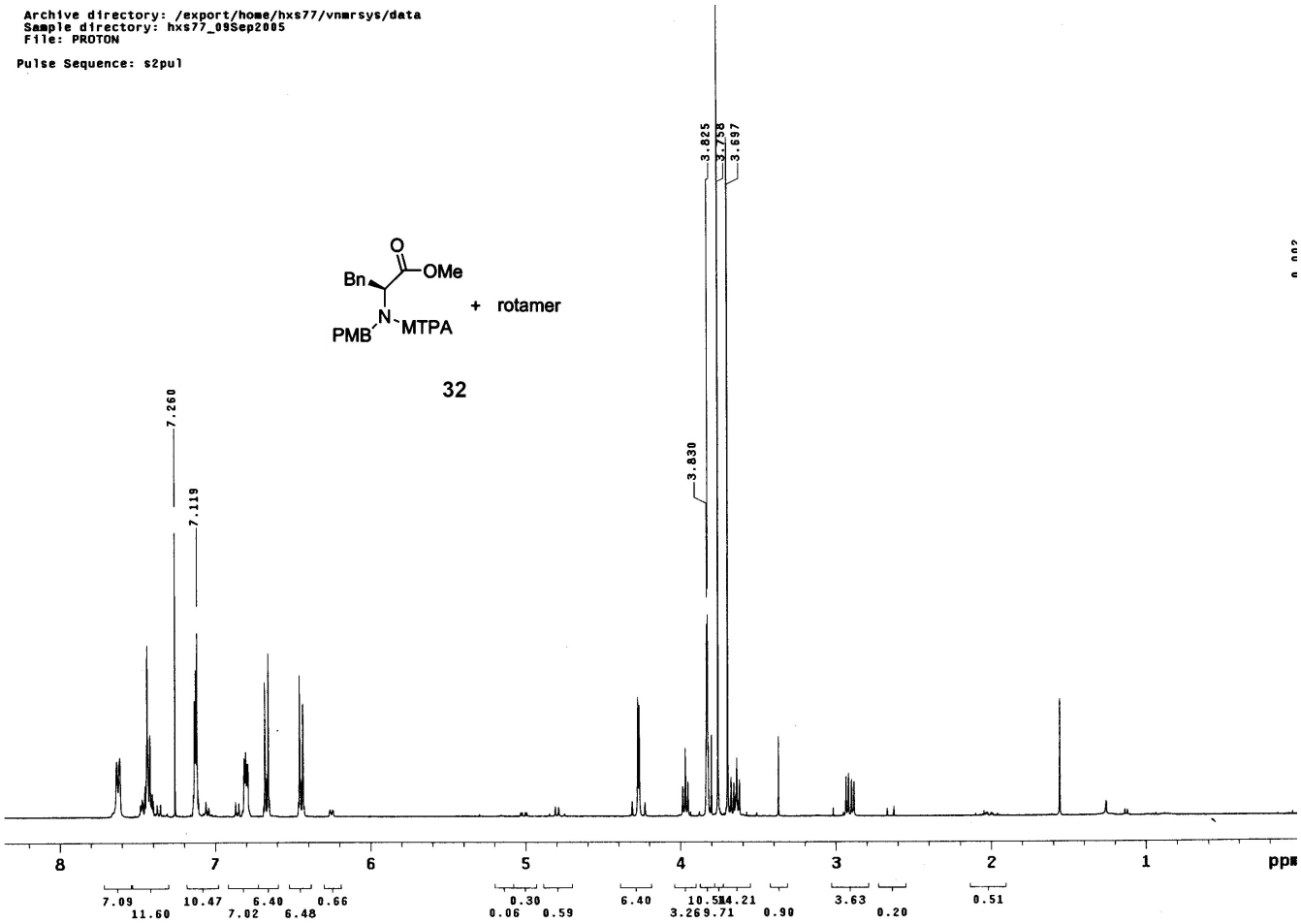


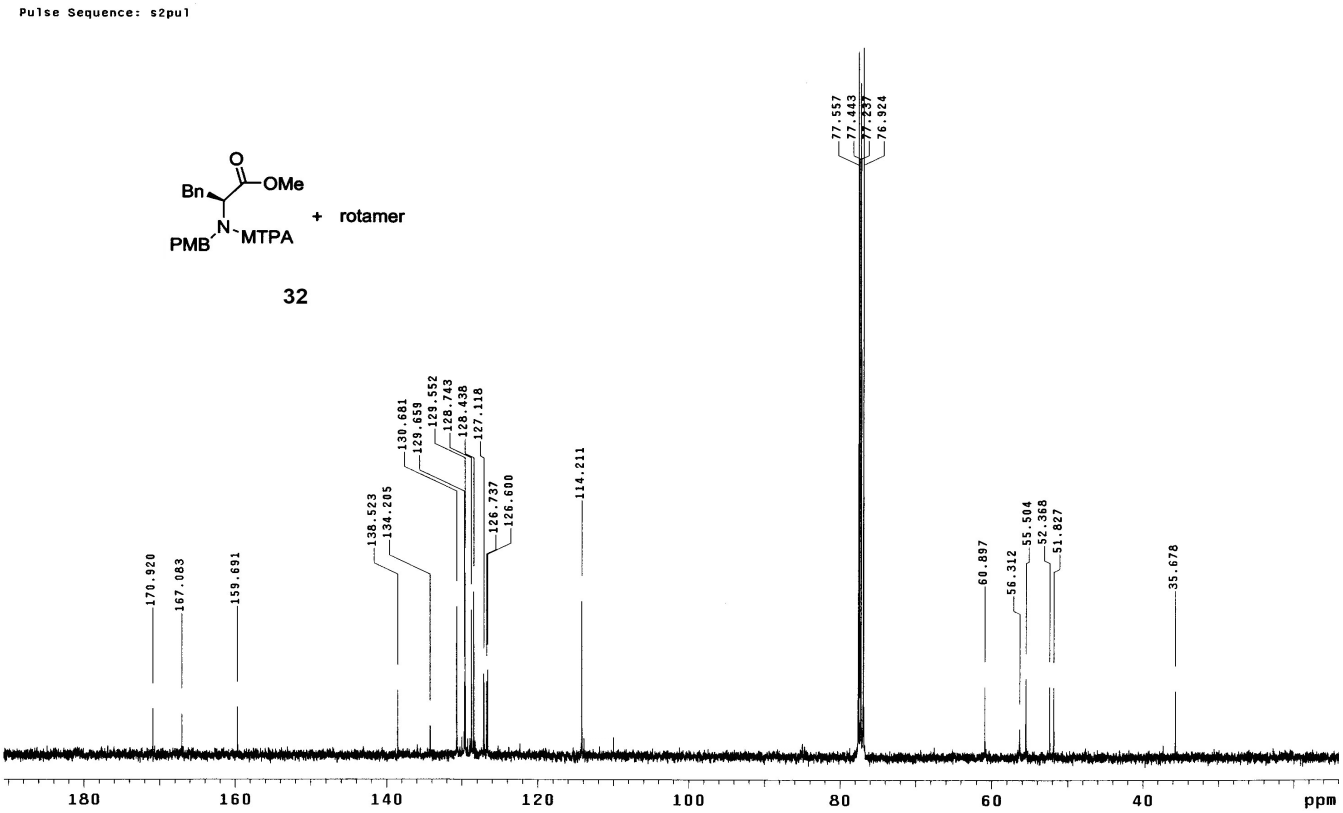


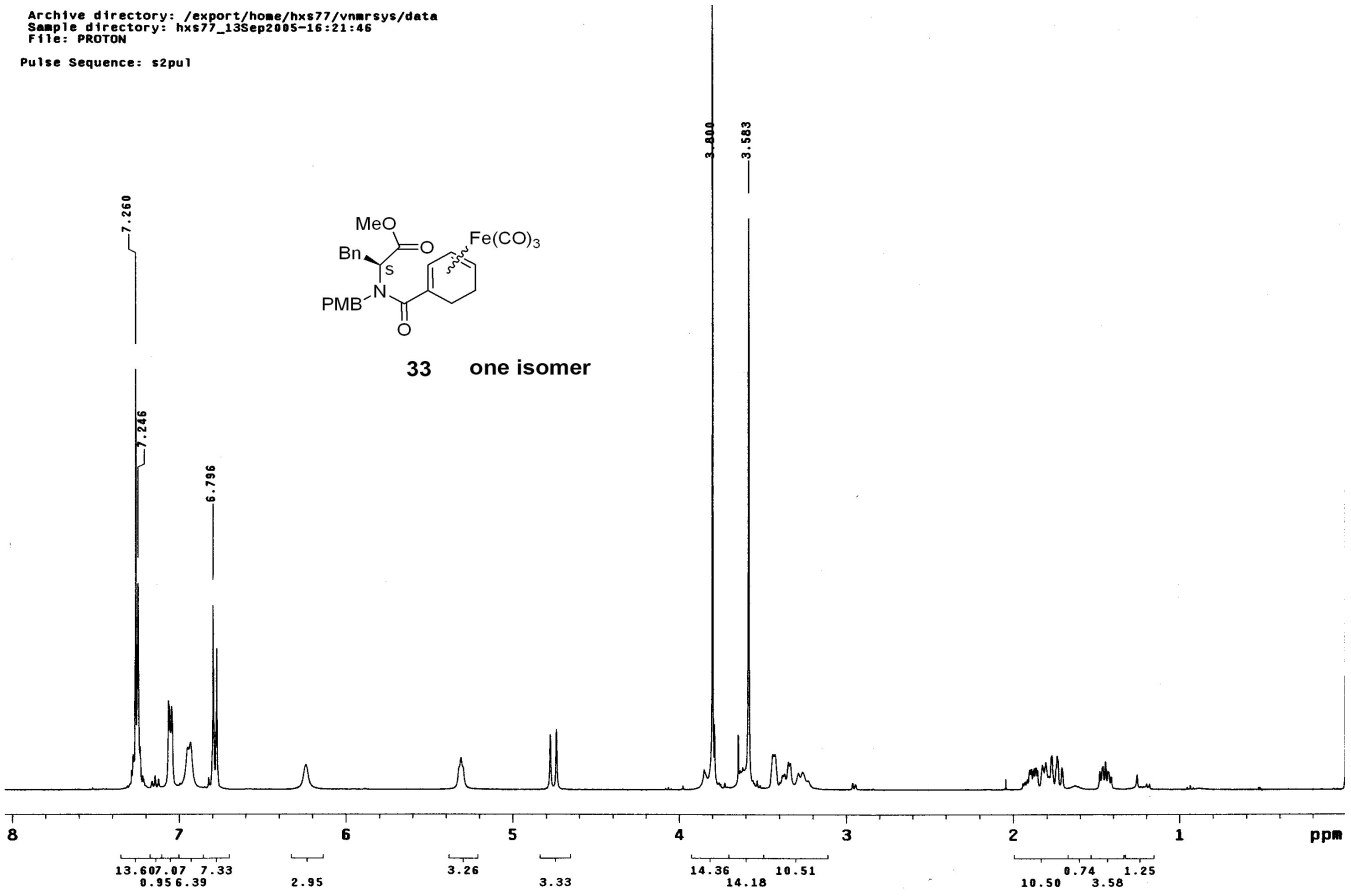

Archive directory: /export/home/hxs77/vnmrsys/data
Sample directory: ReducedDA_08Aug2005
File: CARBON
Pulse Sequence: s2pul
Bn
H
PMB
N
CO2Et
O
23
77.557
77.237
76.916
129.392
129.293
128.178
128.591
126.623
113.899
178.488
177.511
158.868
138.858
61.156
57.296
55.450
46.327
45.816
43.428
41.773
39.980
35.121
26.310
23.747
23.137
20.764
19.124
14.349
200
180
160
140
120
100
80
60
40
20
ppm


Archive directory: /export/home/hxs77/vnmrsys/data
Sample directory: hxs77_17Aug2005-17:22:52
File: PROTON
Pulse Sequence: s2pul
O
OMe
Bn
NH
PMB
31
3.787
3.643
7.256
7.145
6.823
6.801
8
7
6
5
4
3
2
1
ppm
15.38
18.07
9.05
4.839.59
14.18.82
9.53
5.64

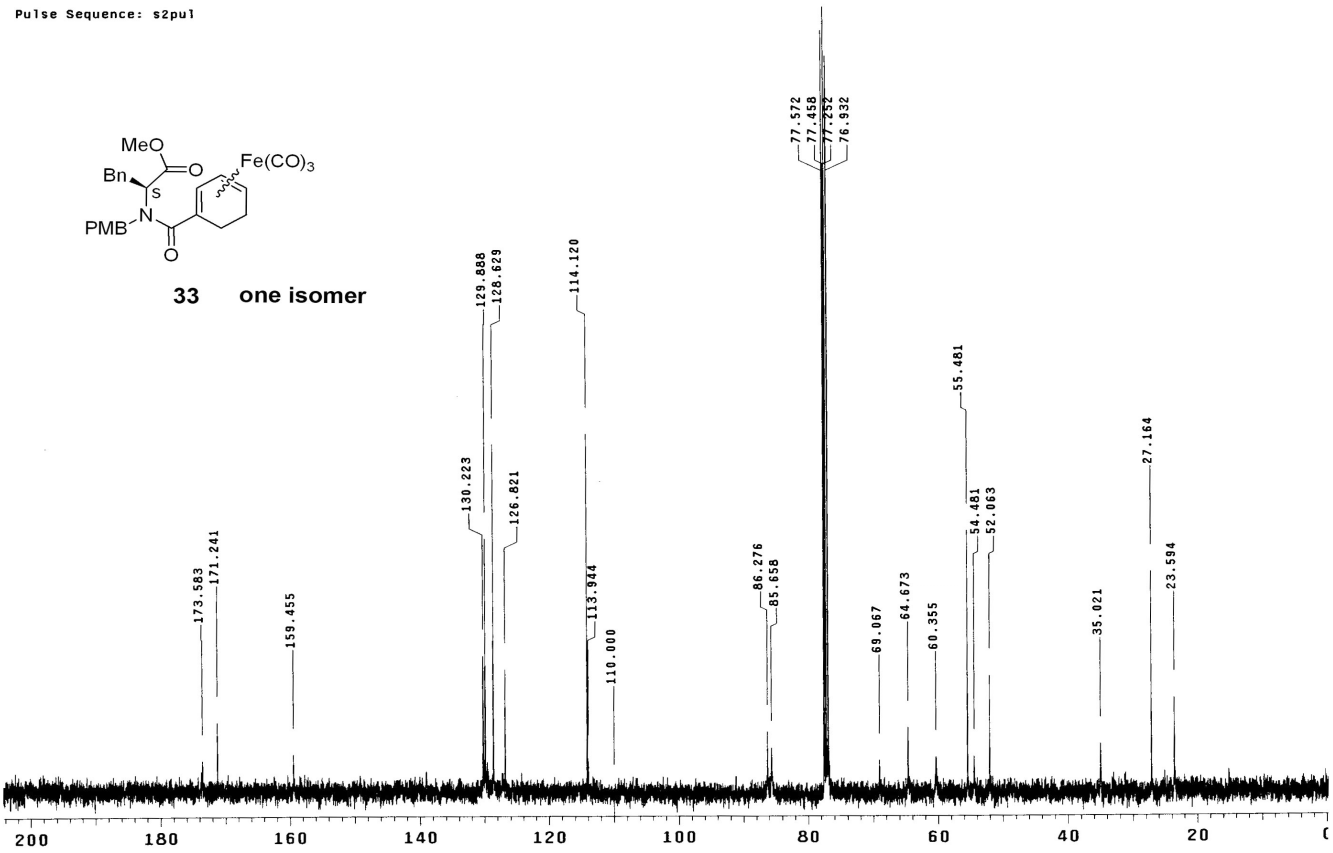

O
OMe
Bn
NH
PMB
31
175.330
158.906
137.569
131.901
129.575
129.437
128.614
126.905
113.952
77.611
77.290
76.970
62.171
55.496
51.880
51.636
39.957
180
160
140
120
100
80
60
40
20
ppm

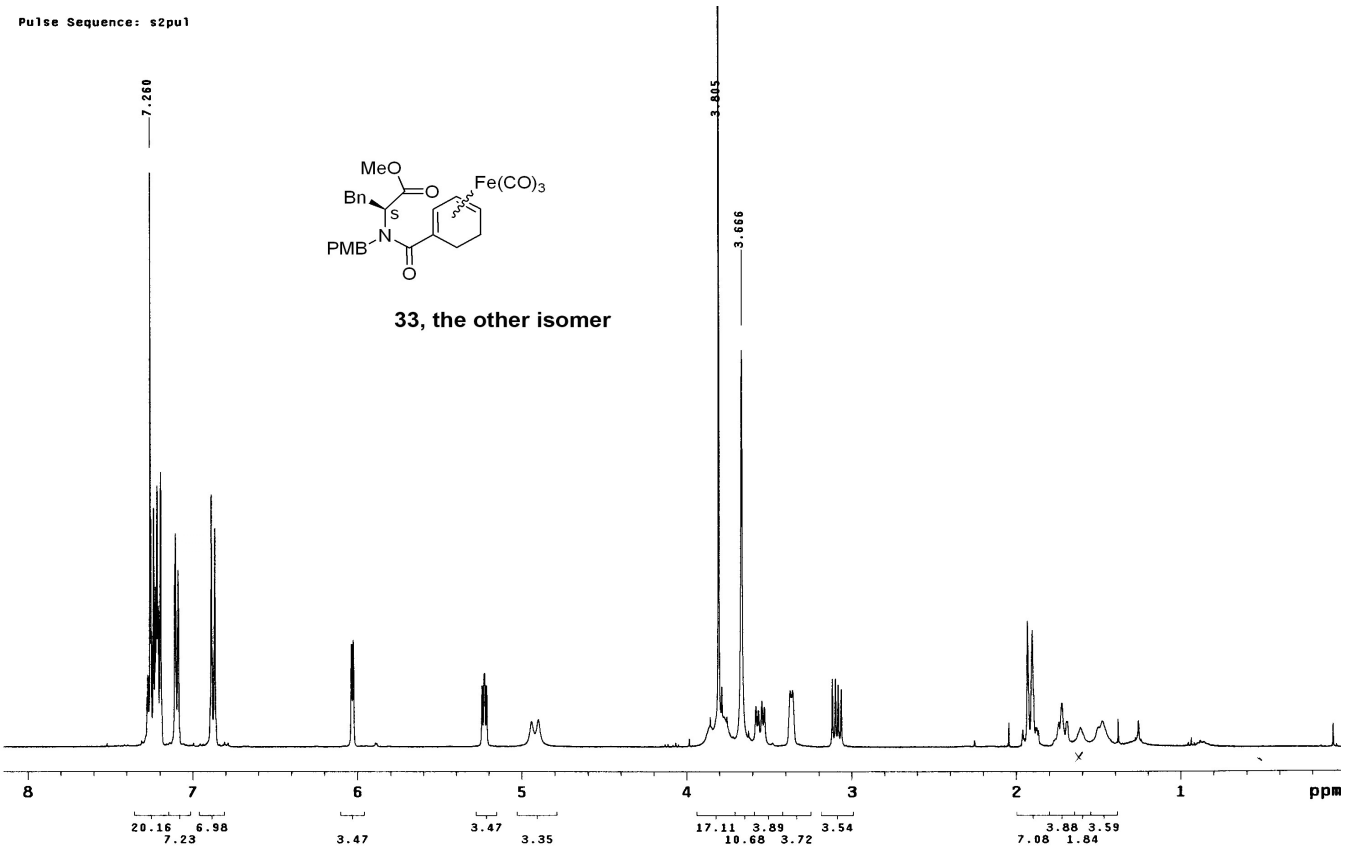

Archive directory: /export/home/hxs77/vnmrsys/data
Sample directory: hxs77_09Sep2005
File: PROTON
Pulse Sequence: s2pul
Bn
OMe
N
PMB
MTPA
+ rotamer
32
7.260
7.119
3.825
3.758
3.697
3.830
8
7
6
5
4
3
2
1
ppm
7.09
11.60
10.47
6.40
7.02
6.48
0.66
0.30
0.06
0.59
6.40
10.51
14.21
3.26
9.71
0.90
3.63
0.20
0.51

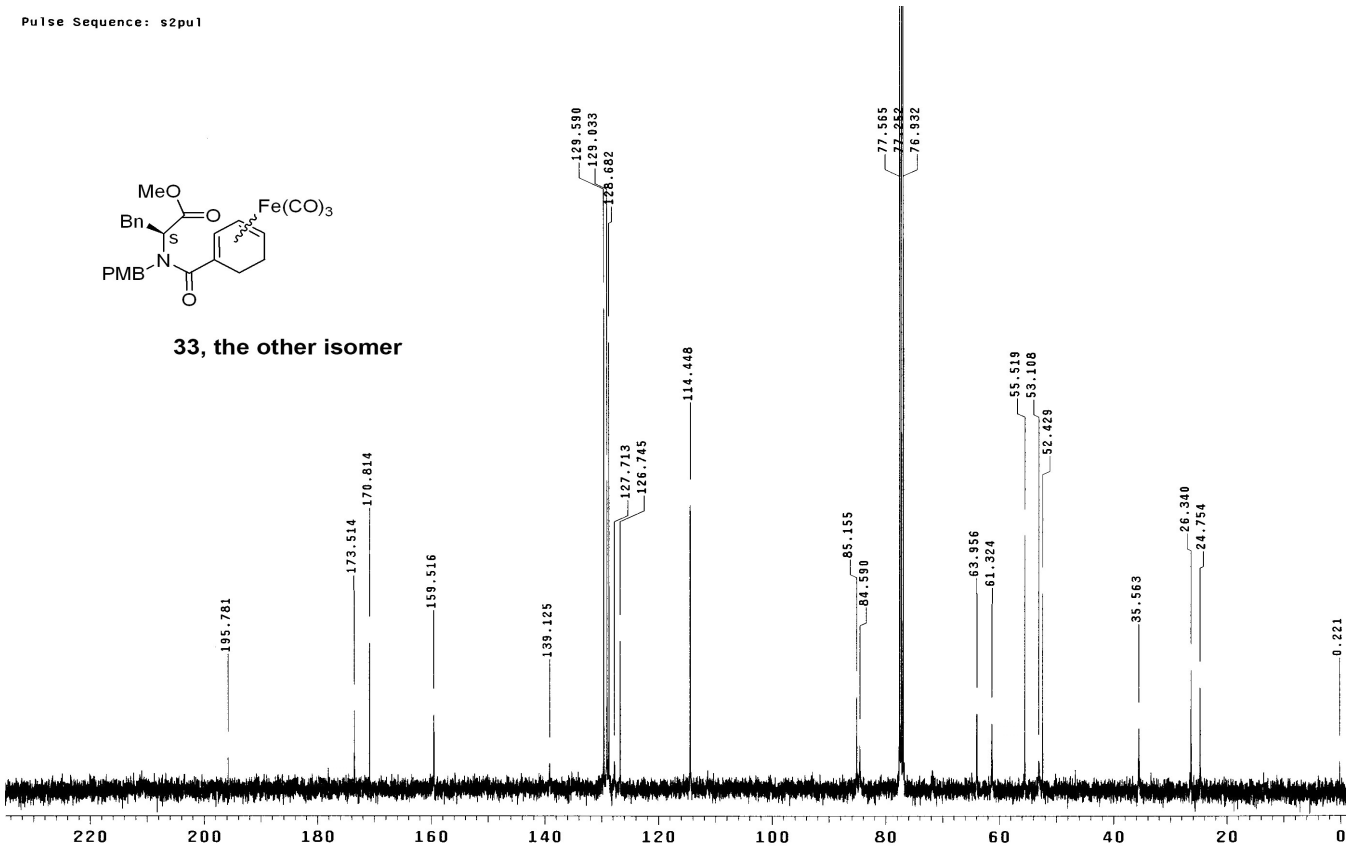

Pulse Sequence: s2pul
Bn
OMe
N
PMB
MTPA
+ rotamer
32
77.557
77.443
77.237
76.924
130.681
129.659
129.552
128.743
128.438
127.118
126.737
126.600
114.211
138.523
134.205
170.920
167.083
159.691
60.897
56.312
55.504
52.368
51.827
35.678
180
160
140
120
100
80
60
40
ppm



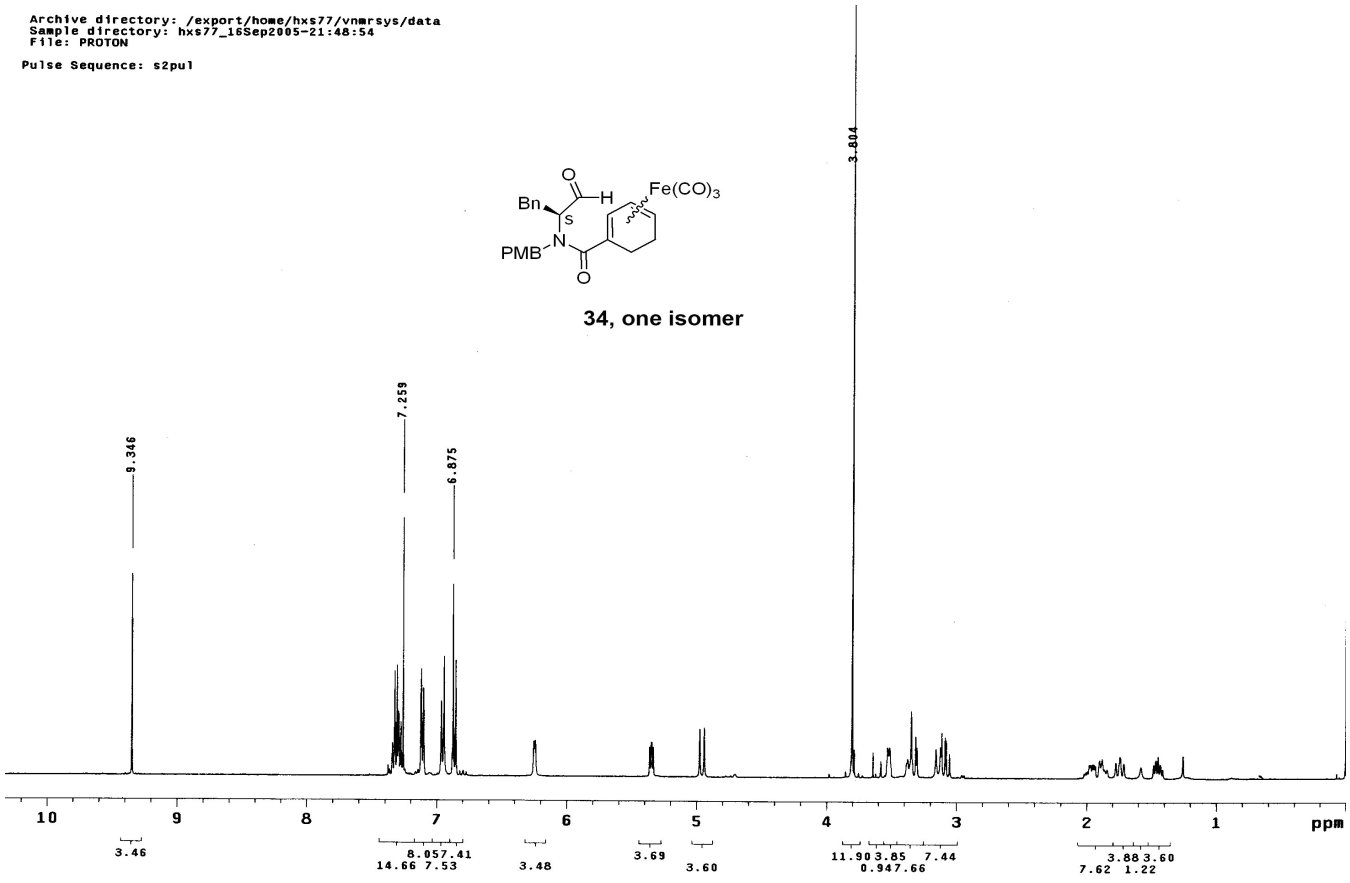
33 **one isomer**


Pulse Sequence: s2pul
MeO
Bn
S
N
PMB
O
O
Fe(CO)3
33 one isomer
77.572
77.458
77.252
76.932
129.888
128.629
114.120
130.223
126.821
55.481
27.164
54.481
52.063
173.583
171.241
159.455
113.944
110.000
86.276
85.658
69.067
64.673
60.355
35.021
23.594
200
180
160
140
120
100
80
60
40
20

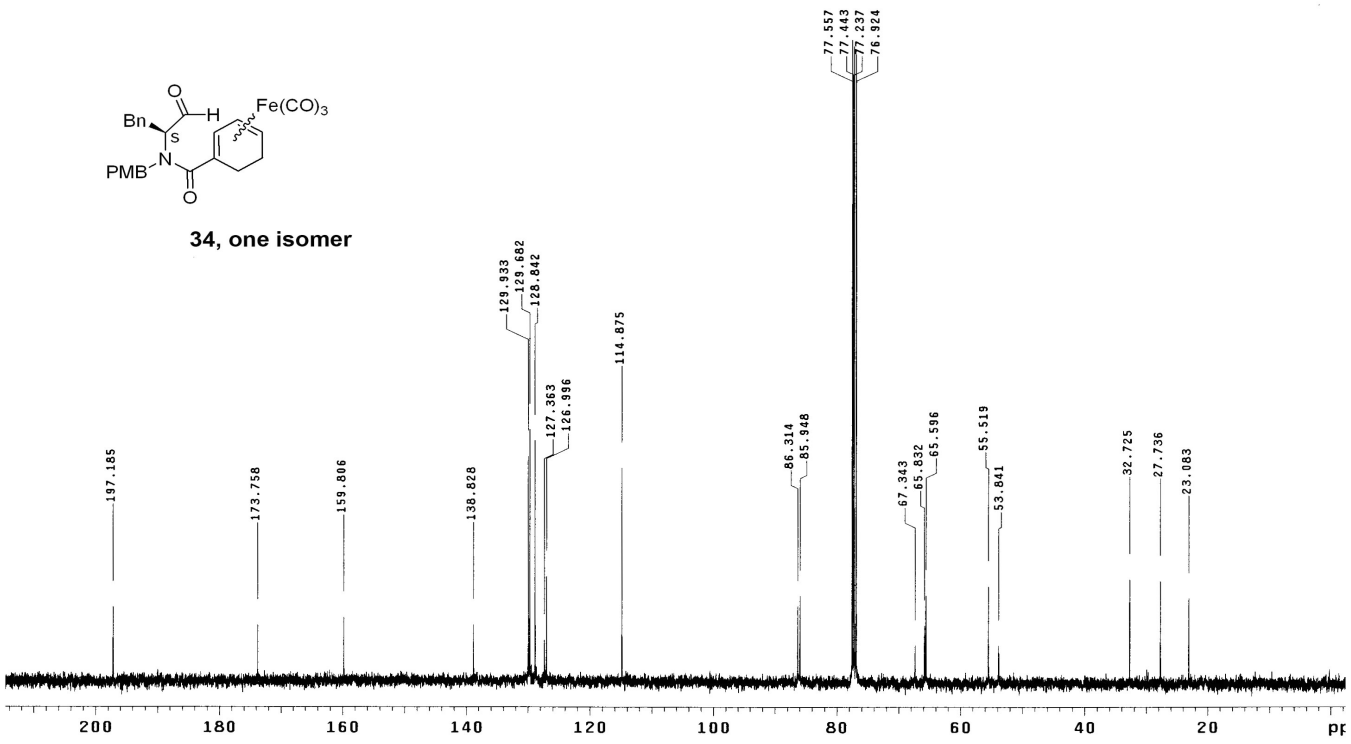

Pulse Sequence: s2pul
7.260
3.805
3.666
MeO
Bn
S
N
PMB
O
O
Fe(CO)3
33, the other isomer
8
7
6
5
4
3
2
1
ppm
20.16
6.98
7.23
3.47
3.47
3.35
17.11
3.89
3.54
10.68
3.72
3.88
3.59
7.08
1.84

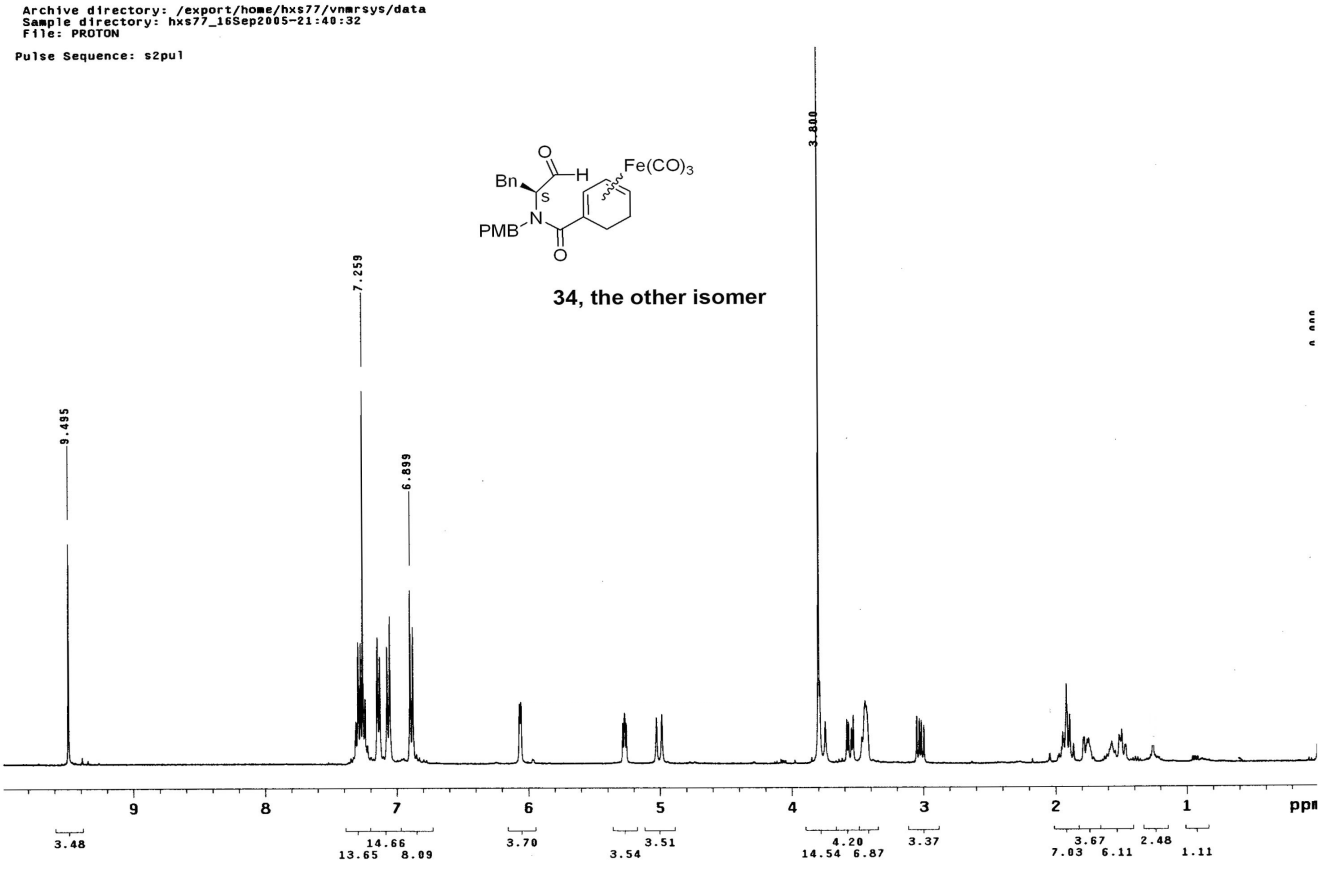


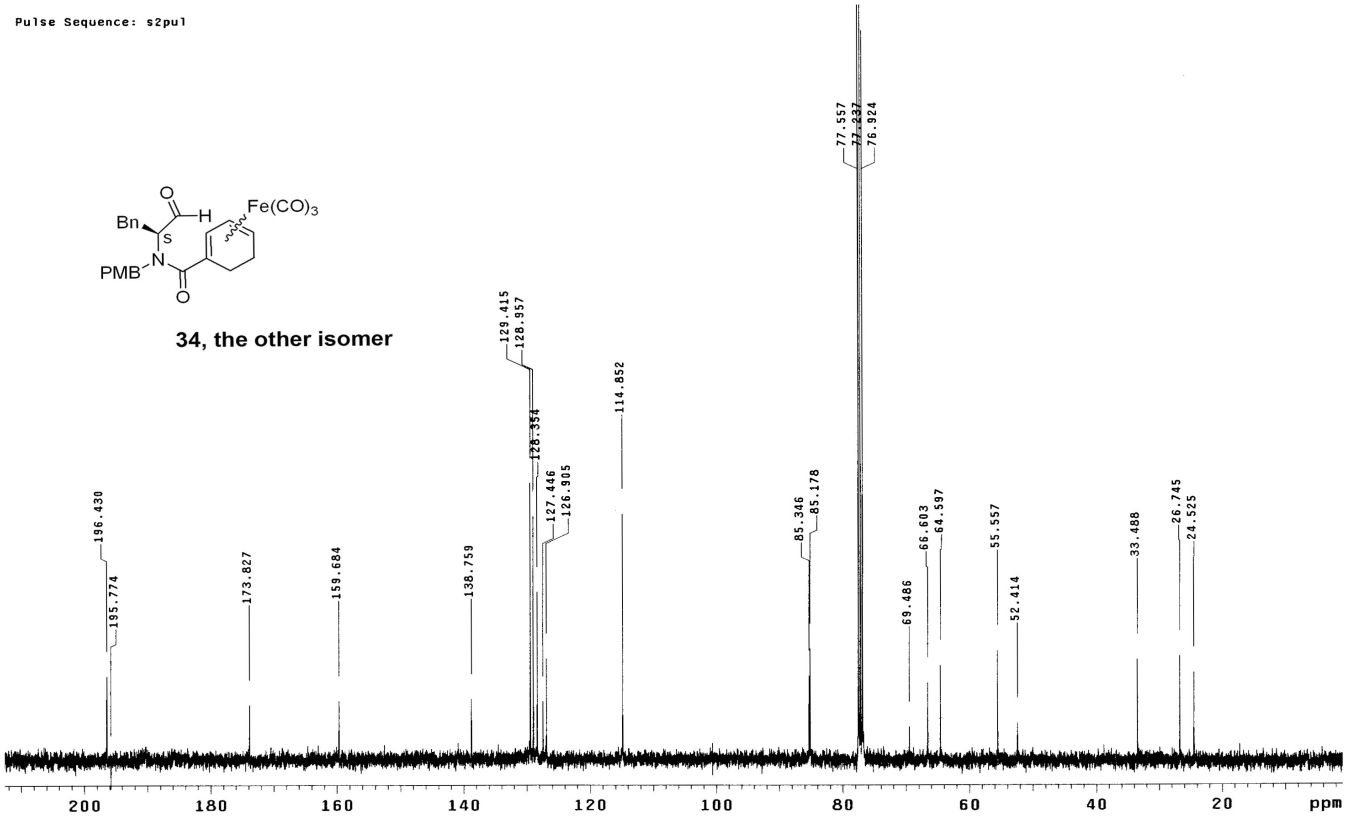
33, the other isomer

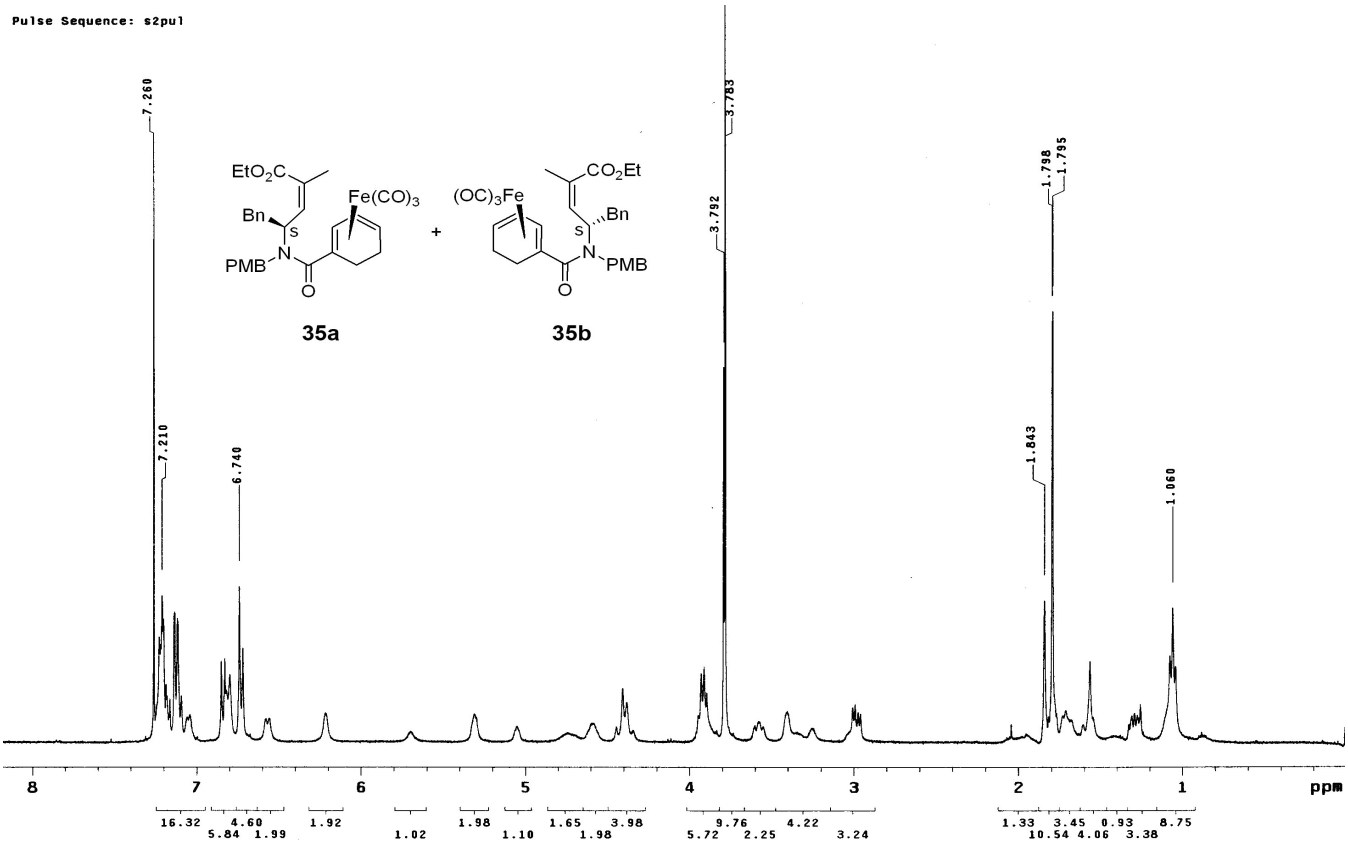


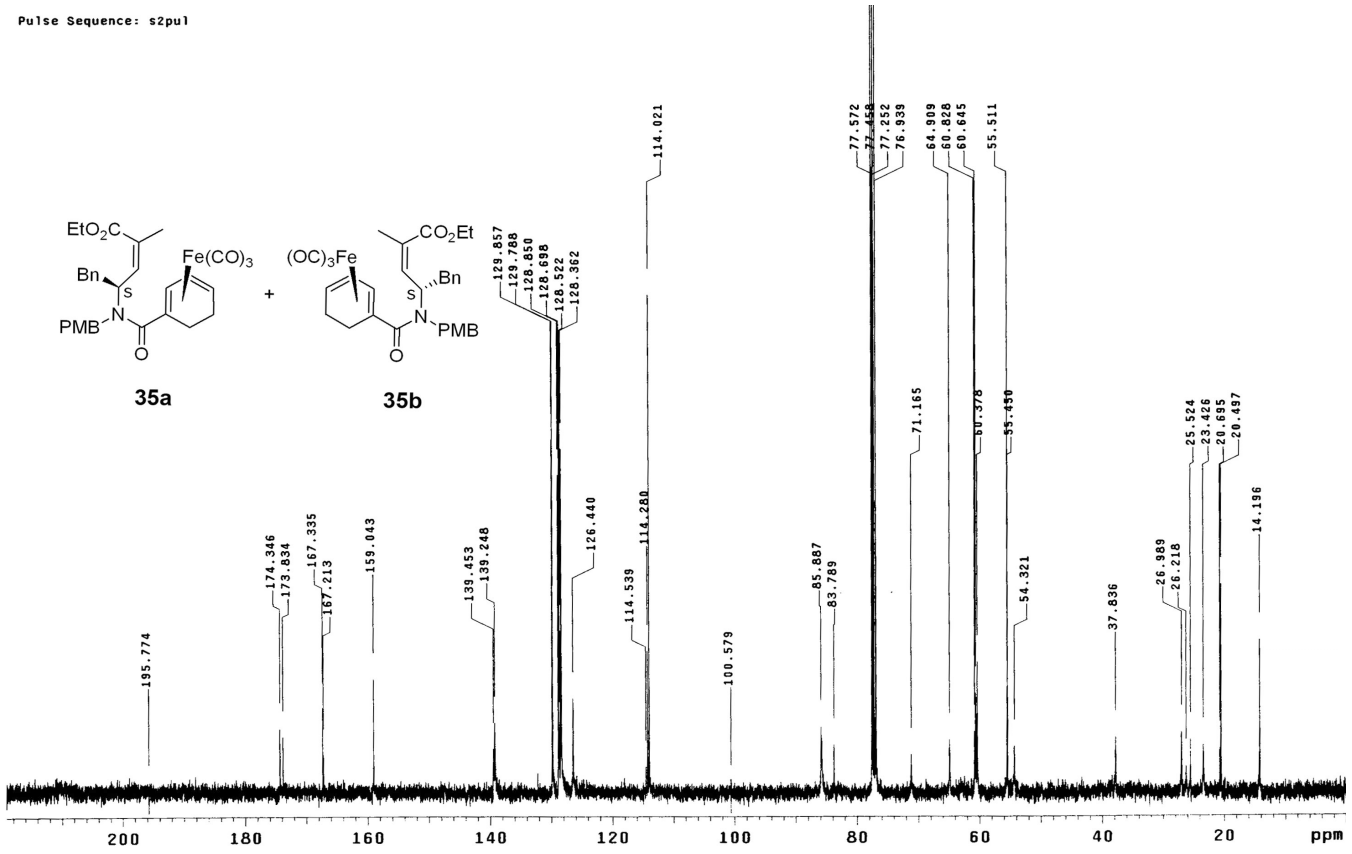
34, one isomer

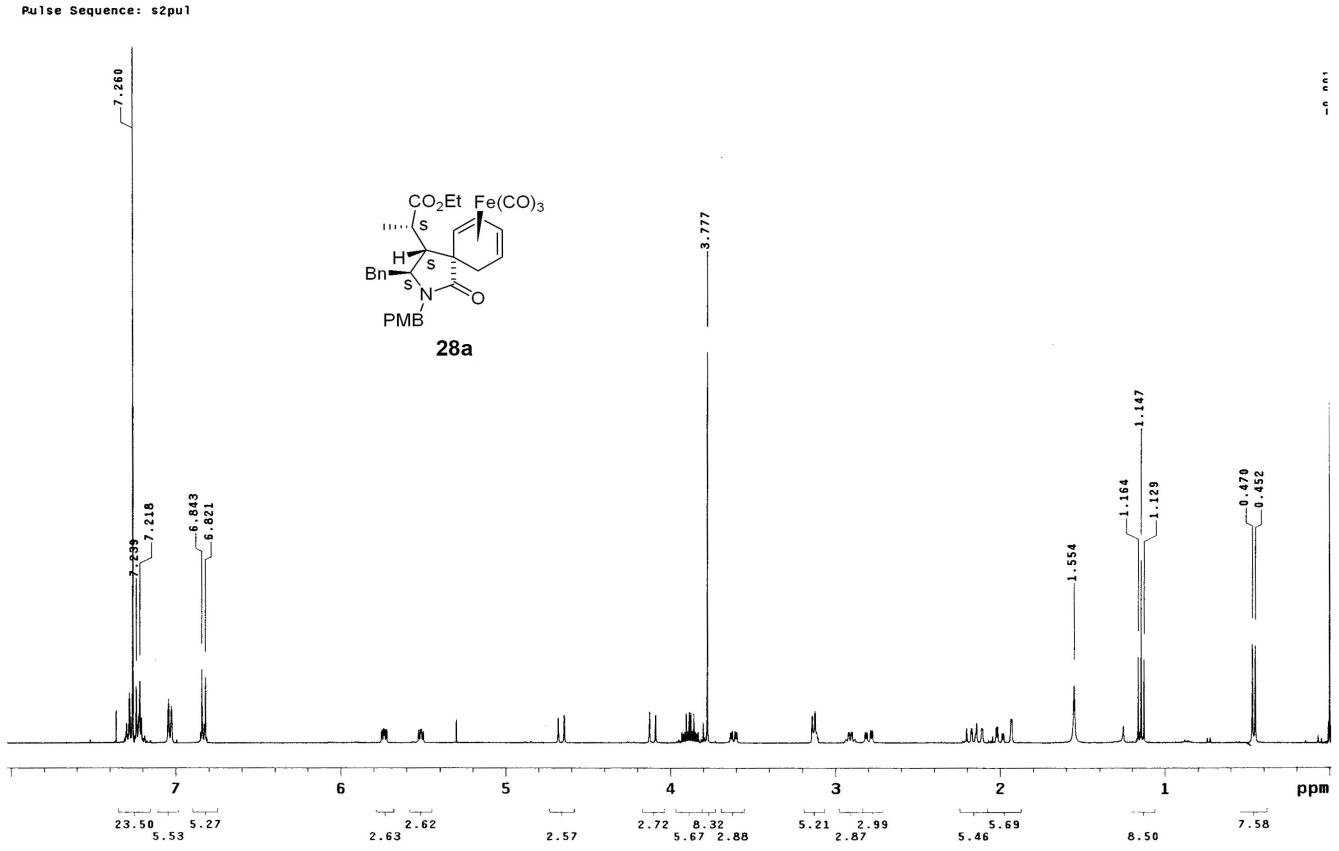

Bn
PMB
Fe(CO)3
34, one isomer
77.557
77.443
77.237
76.924
129.933
129.682
128.842
127.363
126.996
114.875
86.314
85.948
67.343
65.832
65.596
55.519
53.841
32.725
27.736
23.083
197.185
173.758
159.806
138.828
200
180
160
140
120
100
80
60
40
20

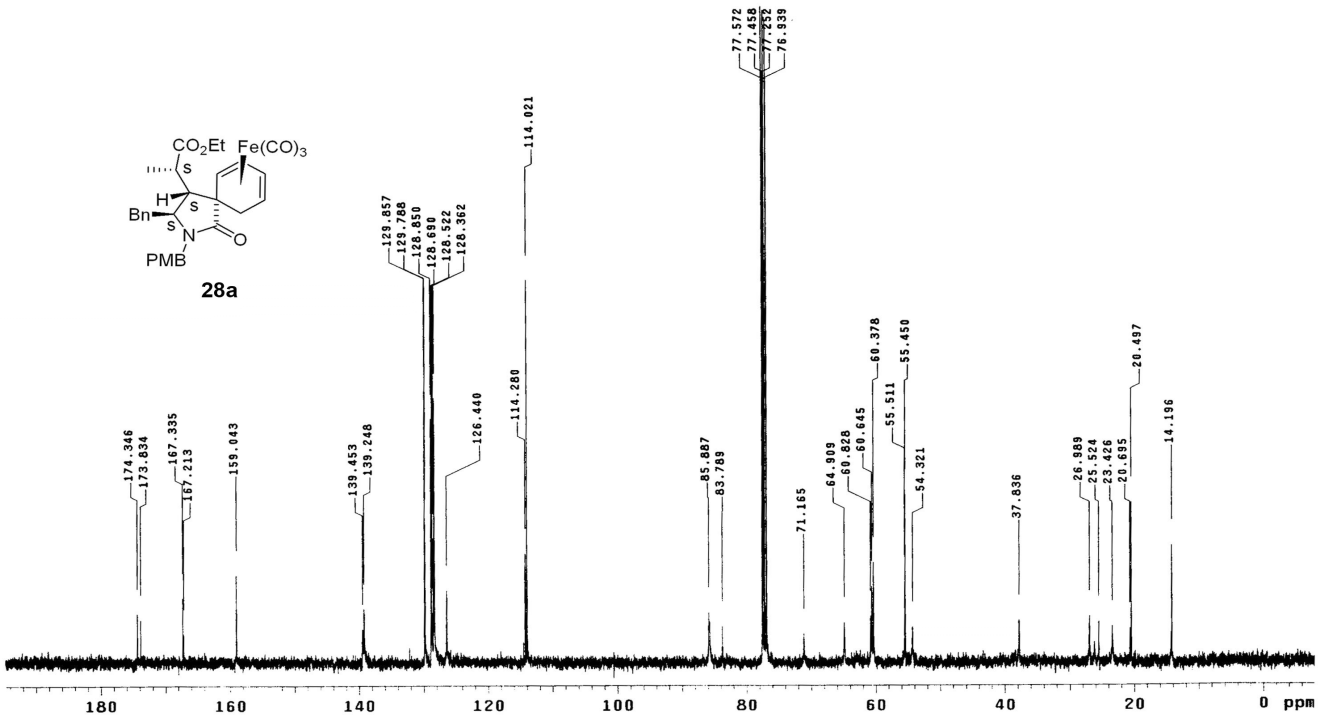

Archive directory: /export/home/hxs77/vnmrsys/data
Sample directory: hxs77_16Sep2005-21:40:32
File: PROTON
Pulse Sequence: s2pul
Bn
PMB
Fe(CO)3
34, the other isomer
9.495
7.259
6.899
3.800
9
8
7
6
5
4
3
2
1
ppm
3.48
14.66
13.65
8.09
3.70
3.54
3.51
4.20
14.54
6.87
3.37
3.67
7.03
6.11
2.48
1.11

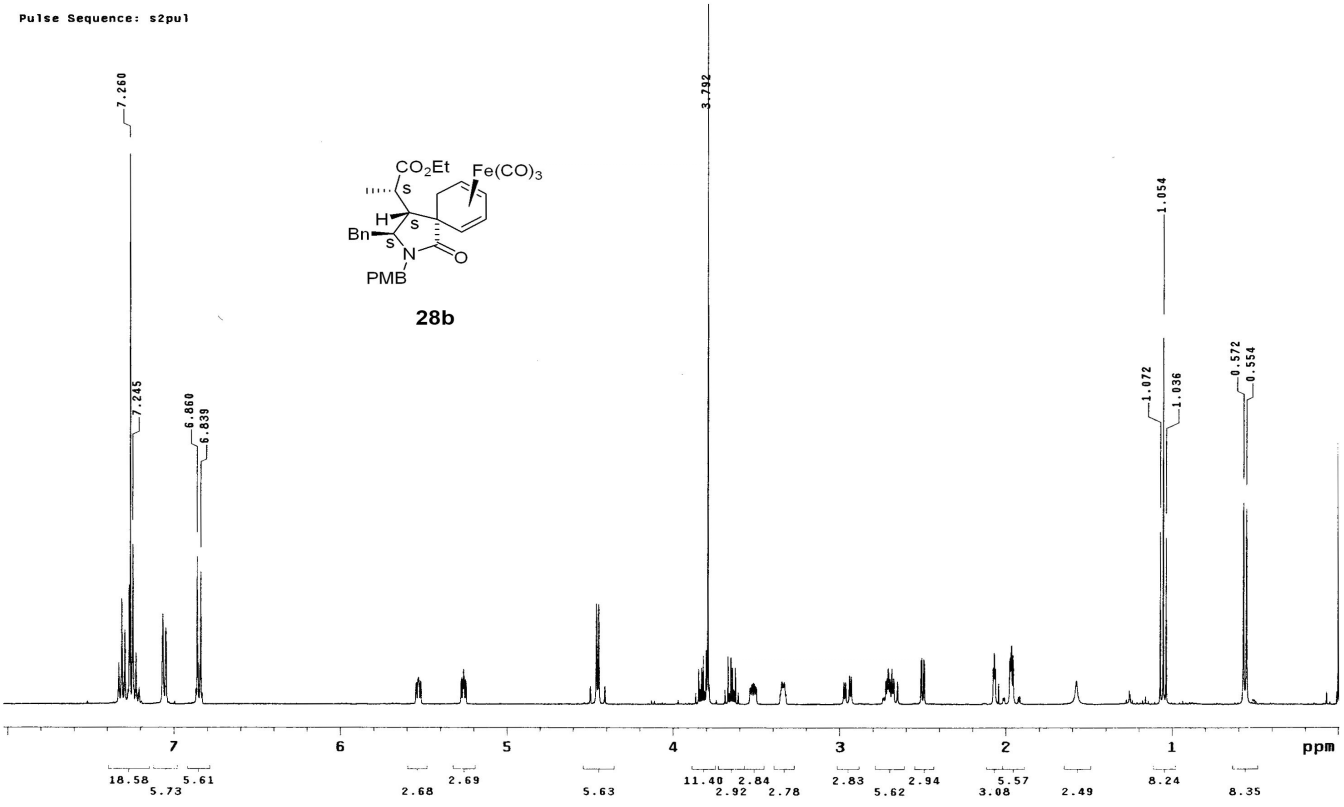

Pulse Sequence: s2pul
Bn
S
N
PMB
O
H
Fe(CO)3
34, the other isomer
77.557
77.237
76.924
129.415
128.957
128.354
127.446
126.905
114.852
85.346
85.178
69.486
66.603
64.597
55.557
52.414
33.488
26.745
24.525
196.430
195.774
173.827
159.684
138.759
200
180
160
140
120
100
80
60
40
20
ppm

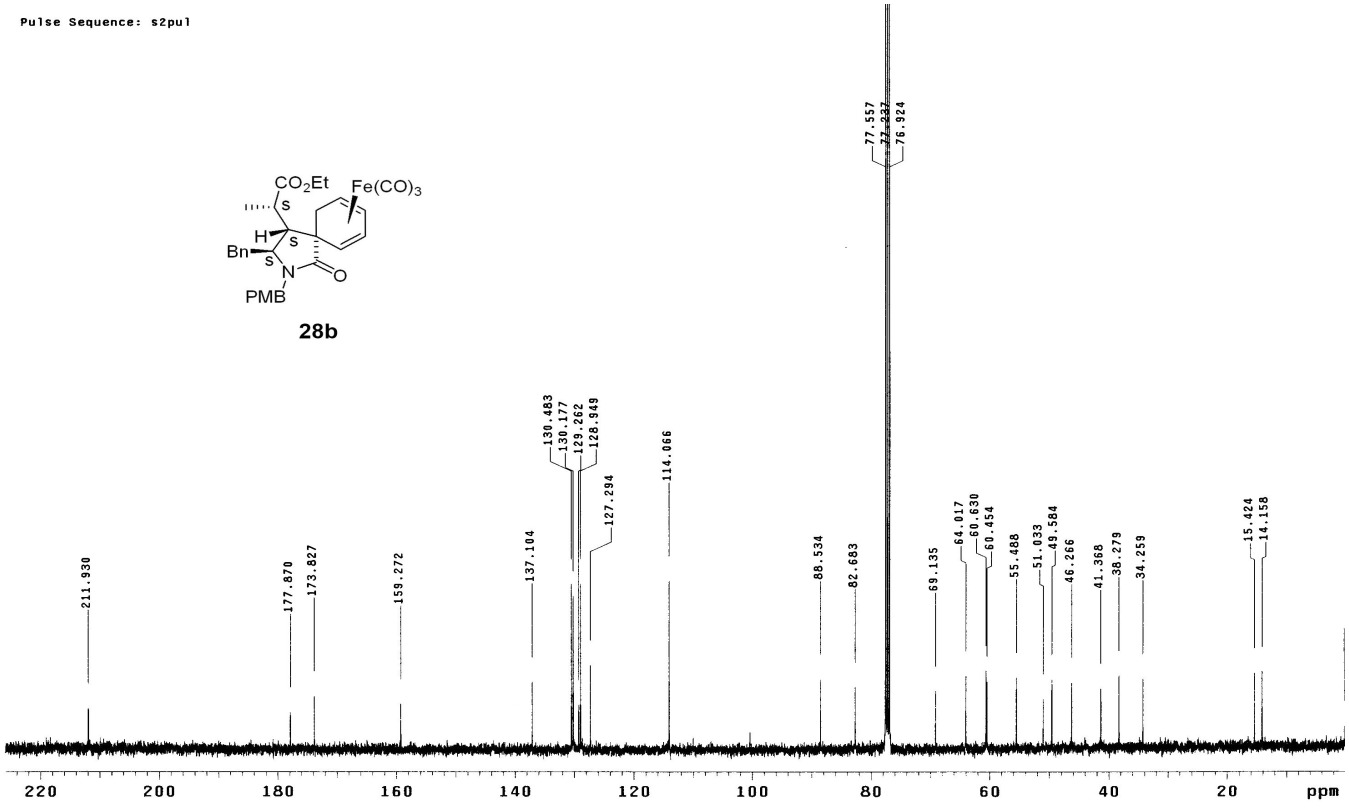

Pulse Sequence: s2pul
7.260
7.210
6.740
3.783
3.792
1.798
1.795
1.843
1.060
EtO2C
Bn
S
N
PMB
O
Fe(CO)3
+
(OC)3Fe
CO2Et
35a
35b
8
7
6
5
4
3
2
1
ppm
16.32
4.60
5.84
1.99
1.92
1.02
1.98
1.10
1.65
3.98
1.98
9.76
5.72
4.22
2.25
3.24
1.33
3.45
0.93
8.75
10.54
4.06
3.38

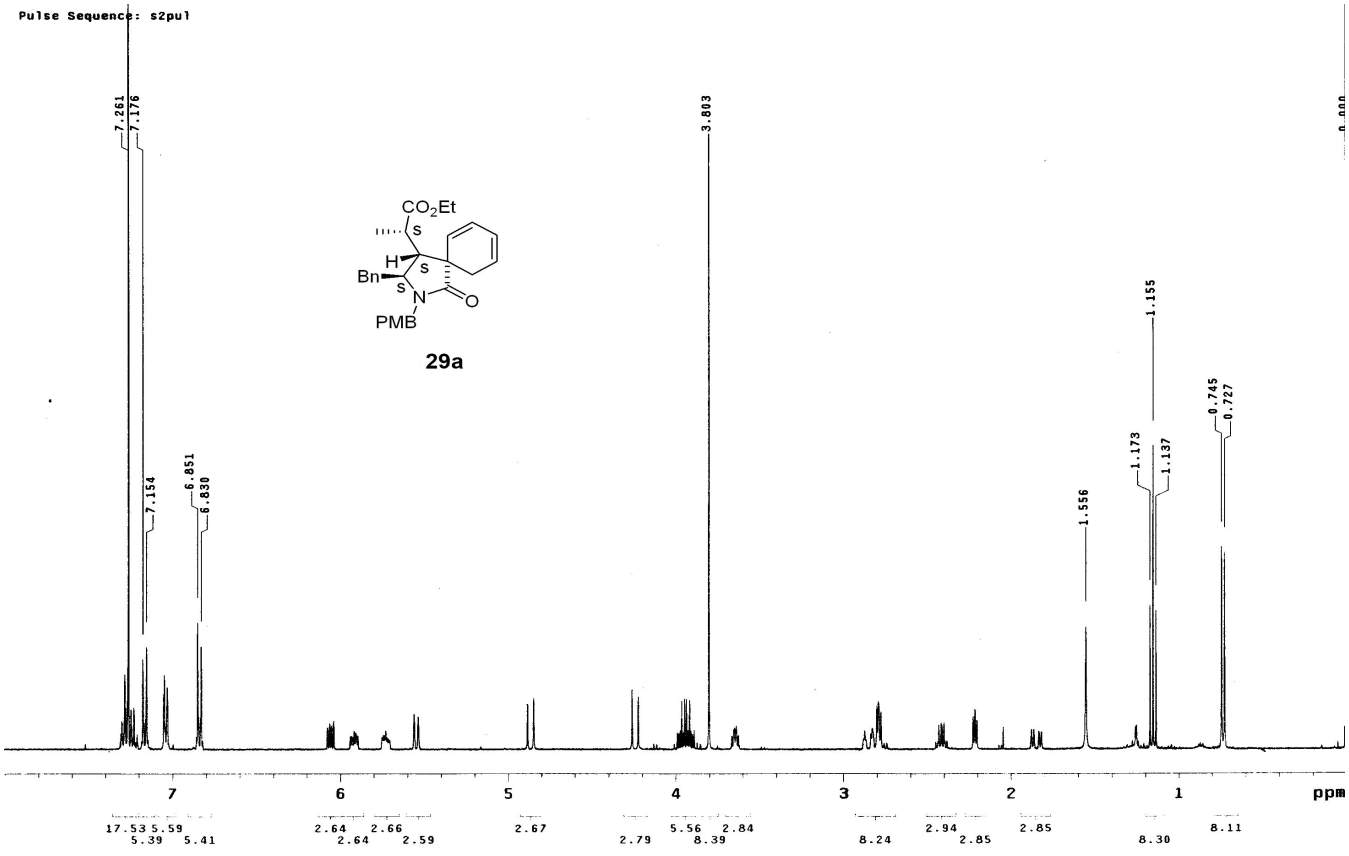

Pulse Sequence: s2pul
35a
35b
195.774
174.346
173.834
167.335
167.213
159.043
139.453
139.248
129.857
129.788
128.850
128.698
128.522
128.362
126.440
114.539
114.280
114.021
100.579
85.887
83.789
77.572
77.458
77.252
76.939
71.165
64.909
60.828
60.645
60.378
55.511
55.450
54.321
37.836
26.989
26.218
25.524
23.426
20.695
20.497
14.196
200
180
160
140
120
100
80
60
40
20
ppm

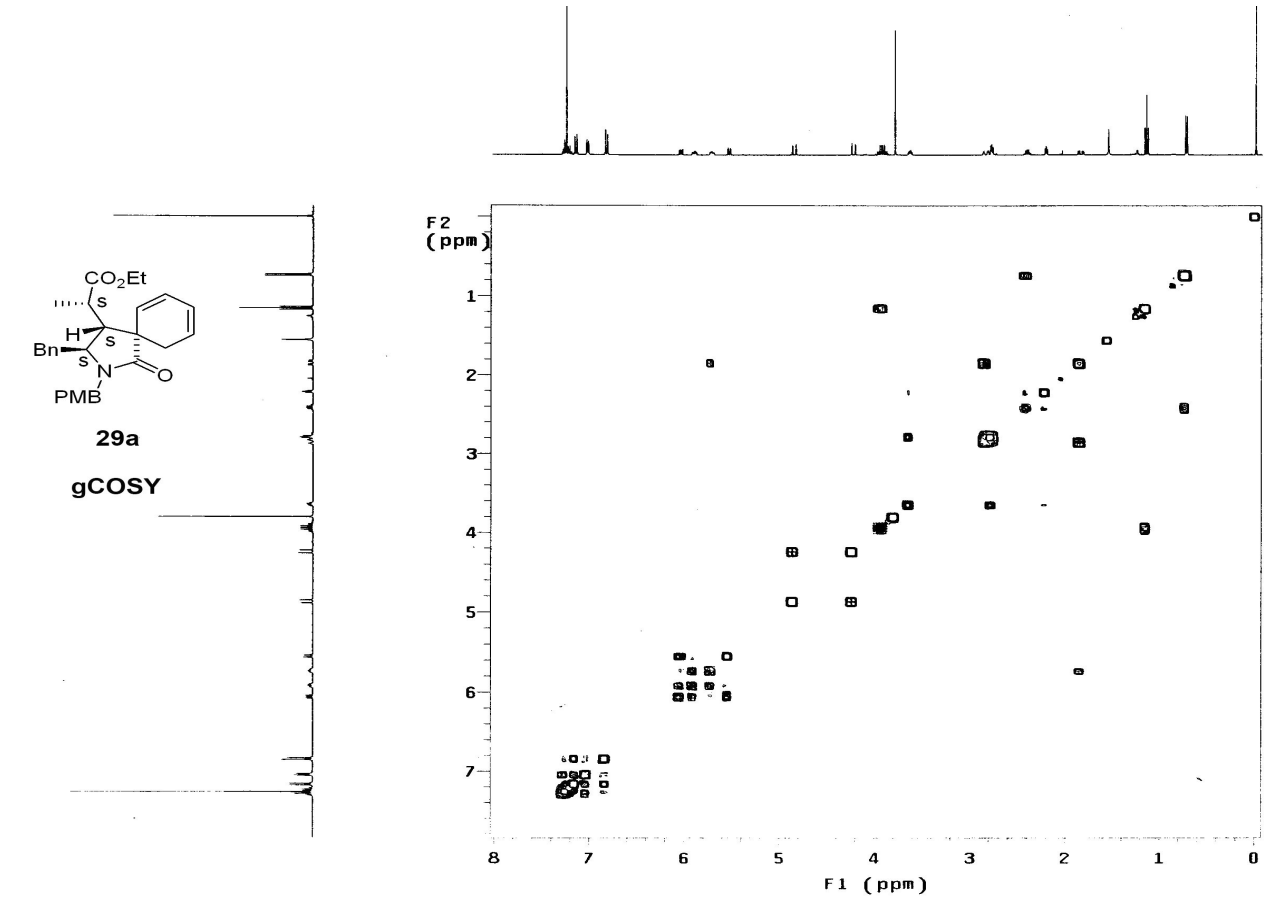

Pulse Sequence: s2pul
28a
7.260
7.239
7.218
6.843
6.821
3.777
1.554
1.164
1.147
1.129
0.470
0.452
7
6
5
4
3
2
1
ppm
23.50
5.53
5.27
2.63
2.62
2.57
2.72
8.32
5.67
2.88
5.21
2.99
2.87
5.46
5.69
8.50
7.58

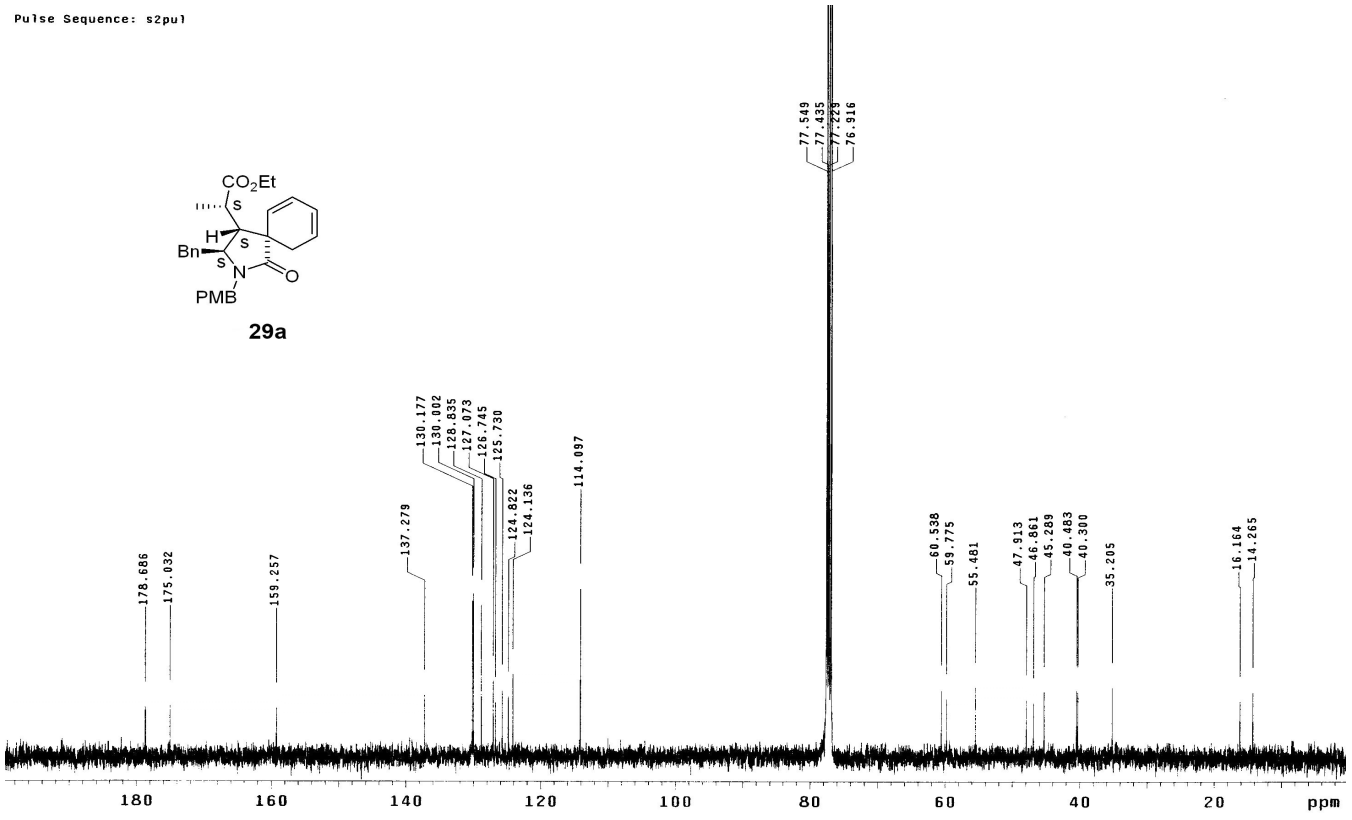

CO2Et
Fe(CO)3
H
Bn
N
O
PMB
28a
77.572
77.458
77.252
76.939
129.857
129.788
128.850
128.690
128.522
128.362
114.021
174.346
173.834
167.335
167.213
159.043
139.453
139.248
126.440
114.280
85.887
83.789
71.165
64.909
60.828
60.645
60.378
55.511
55.450
54.321
37.836
26.989
25.524
23.426
20.695
20.497
14.196
180
160
140
120
100
80
60
40
20
0 ppm

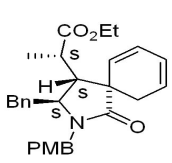

Pulse Sequence: s2pul
CO2Et
Fe(CO)3
H
Bn
N
O
PMB
28b
7.260
7.245
6.860
6.839
3.792
1.054
1.072
1.036
0.572
0.554
7
6
5
4
3
2
1
ppm
18.58
5.73
5.61
2.68
2.69
5.63
11.40
2.84
2.92
2.78
2.83
5.62
2.94
5.57
3.08
2.49
8.24
8.35


Pulse Sequence: s2pul
CO2Et
Fe(CO)3
H
Bn
N
O
PMB
28b
211.930
177.870
173.827
159.272
137.104
130.483
130.177
129.262
128.949
127.294
114.066
88.534
82.683
77.557
77.232
76.924
69.135
64.017
60.630
60.454
55.488
51.033
49.584
46.266
41.368
38.279
34.259
15.424
14.158
220
200
180
160
140
120
100
80
60
40
20
ppm


Pulse Sequence: s2pul
CO2Et
H
Bn
N
O
PMB
29a
7.261
7.176
7.154
6.851
6.830
3.803
1.556
1.173
1.155
1.137
0.745
0.727
7
6
5
4
3
2
1
ppm
17.53
5.59
5.39
5.41
2.64
2.64
2.66
2.64
2.59
2.67
2.79
5.56
8.39
2.84
8.24
2.94
2.85
2.85
8.30
8.11

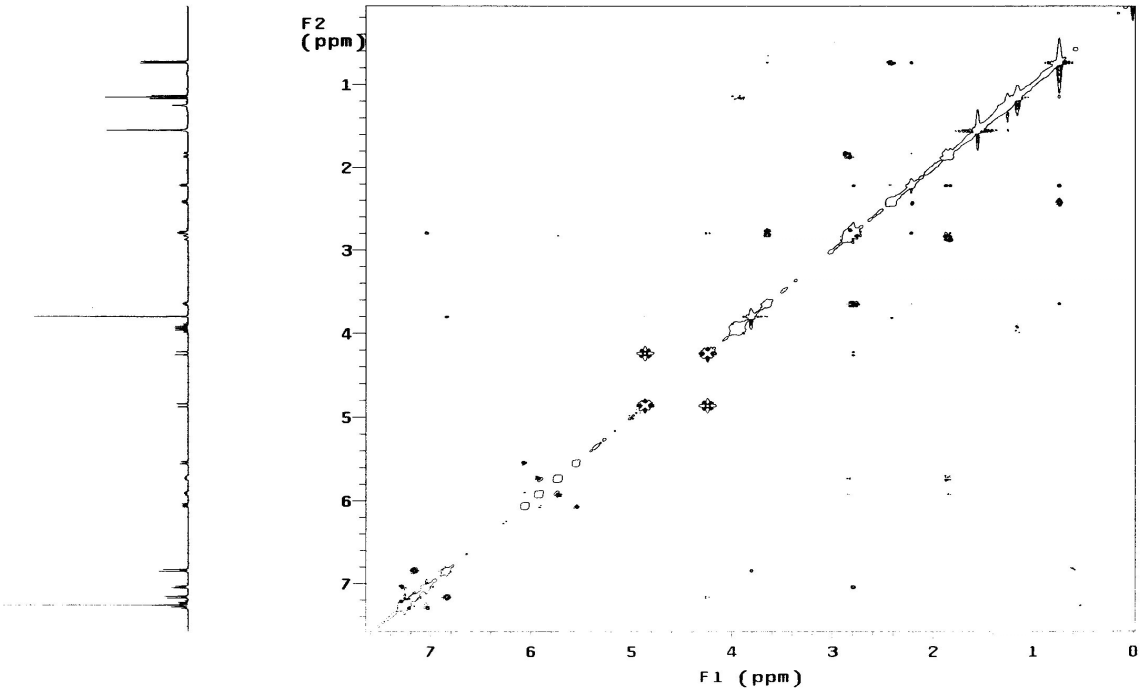

CO2Et
H
Bn
N
O
PMB
29a
gCOSY
F2 (ppm)
F1 (ppm)

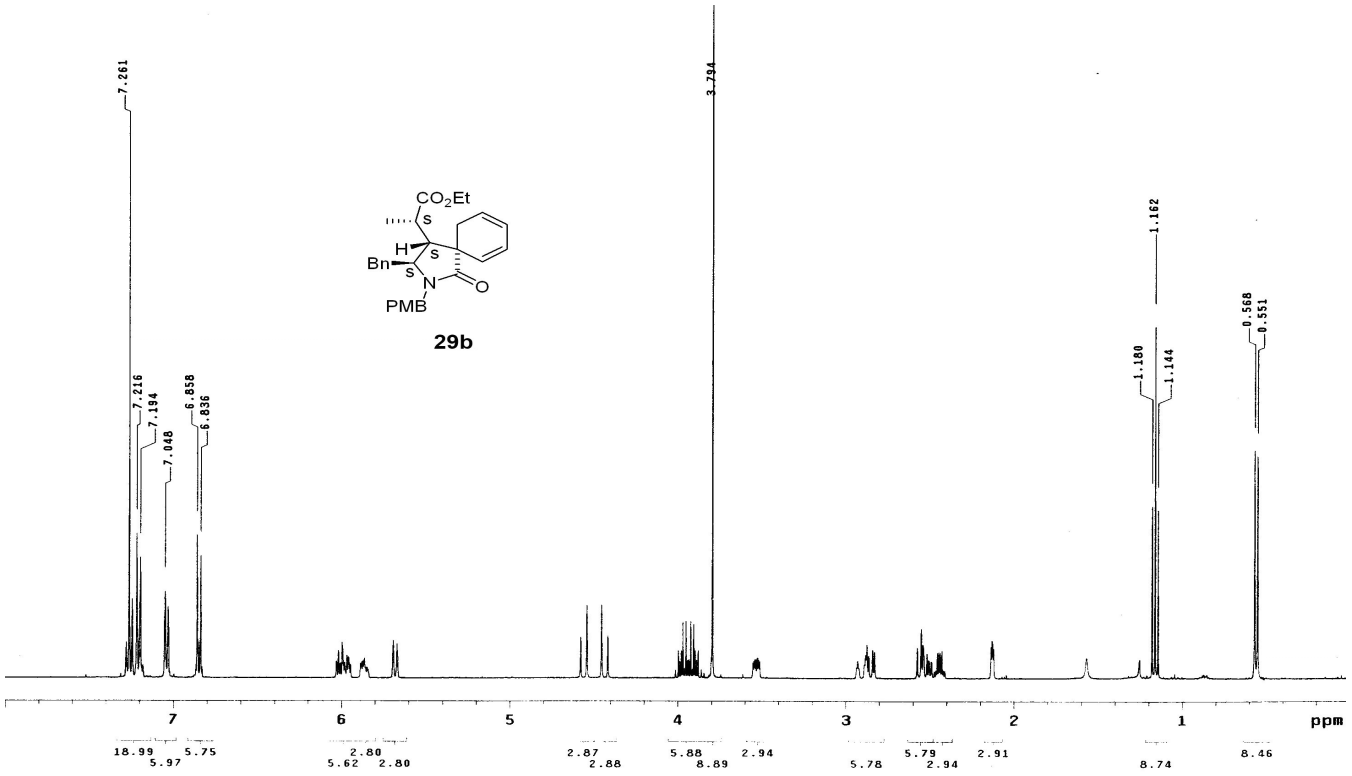

Pulse Sequence: s2pul
CO2Et
H
Bn
N
O
PMB
29a
178.686
175.032
159.257
137.279
130.177
130.002
128.835
127.073
126.745
125.730
124.822
124.136
114.097
77.549
77.435
77.229
76.916
60.538
59.775
55.481
47.913
46.861
45.289
40.483
40.300
35.205
16.164
14.265
ppm

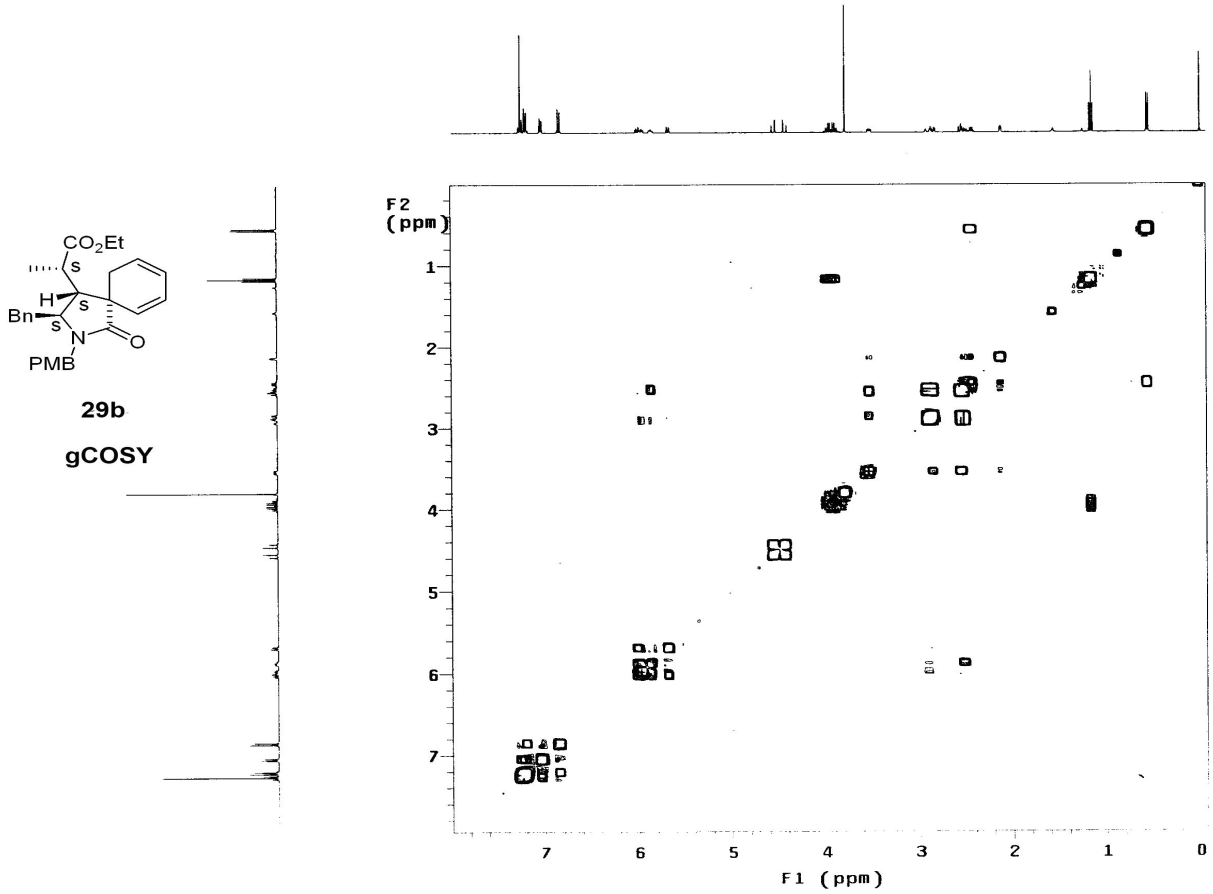


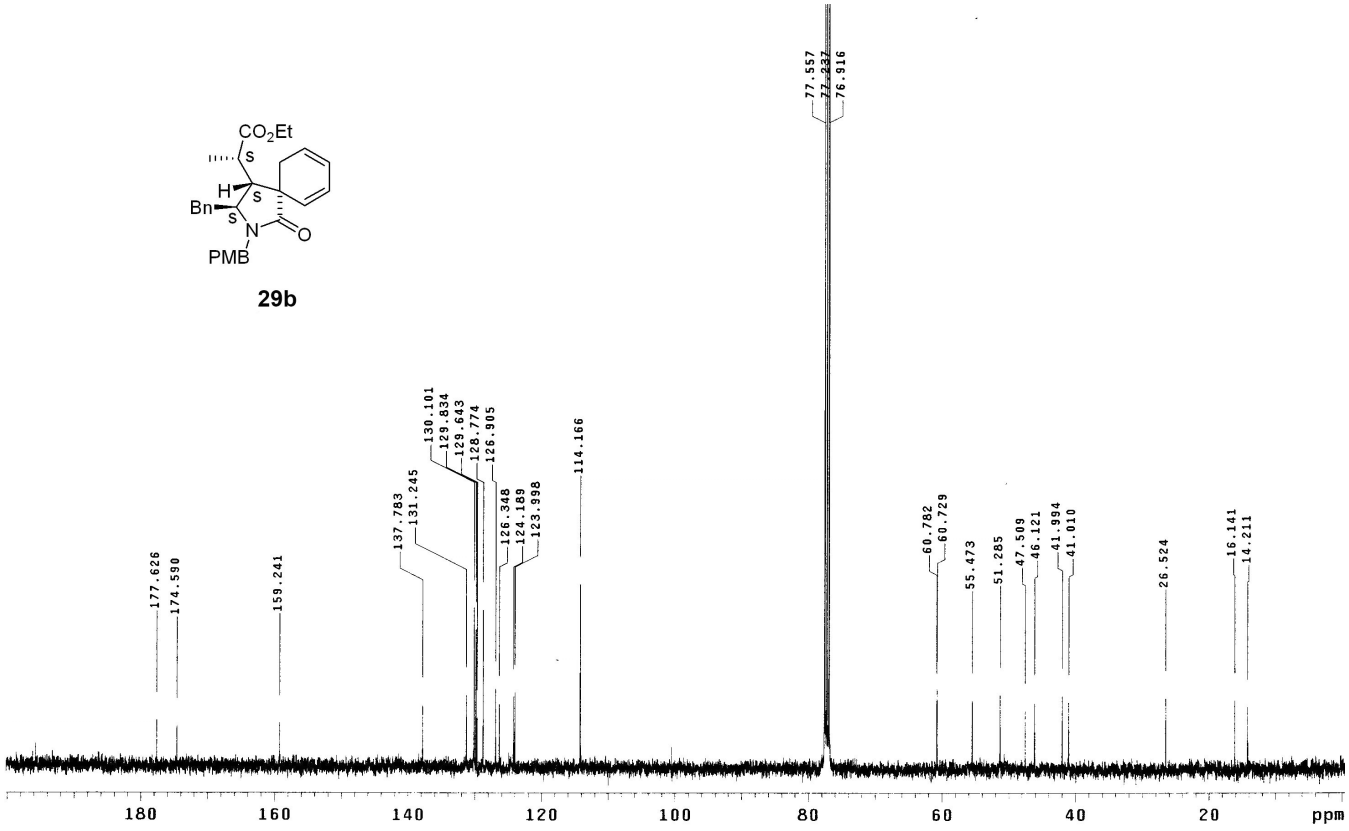
29a

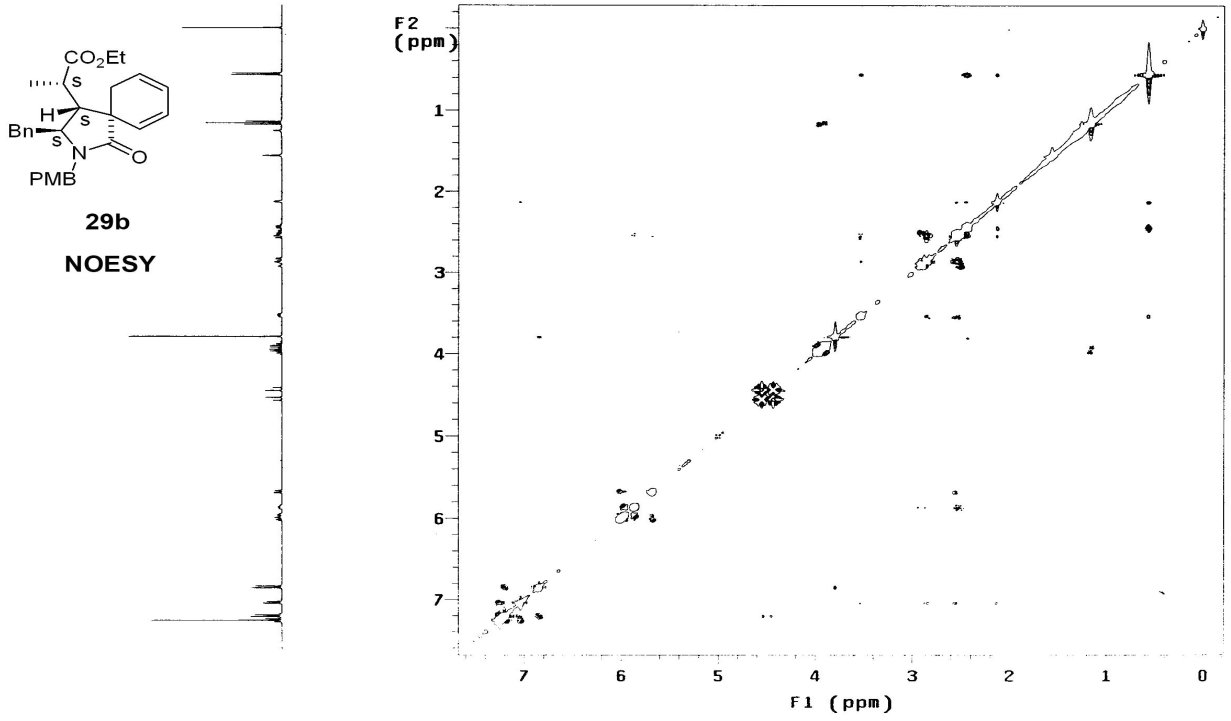
NOESY

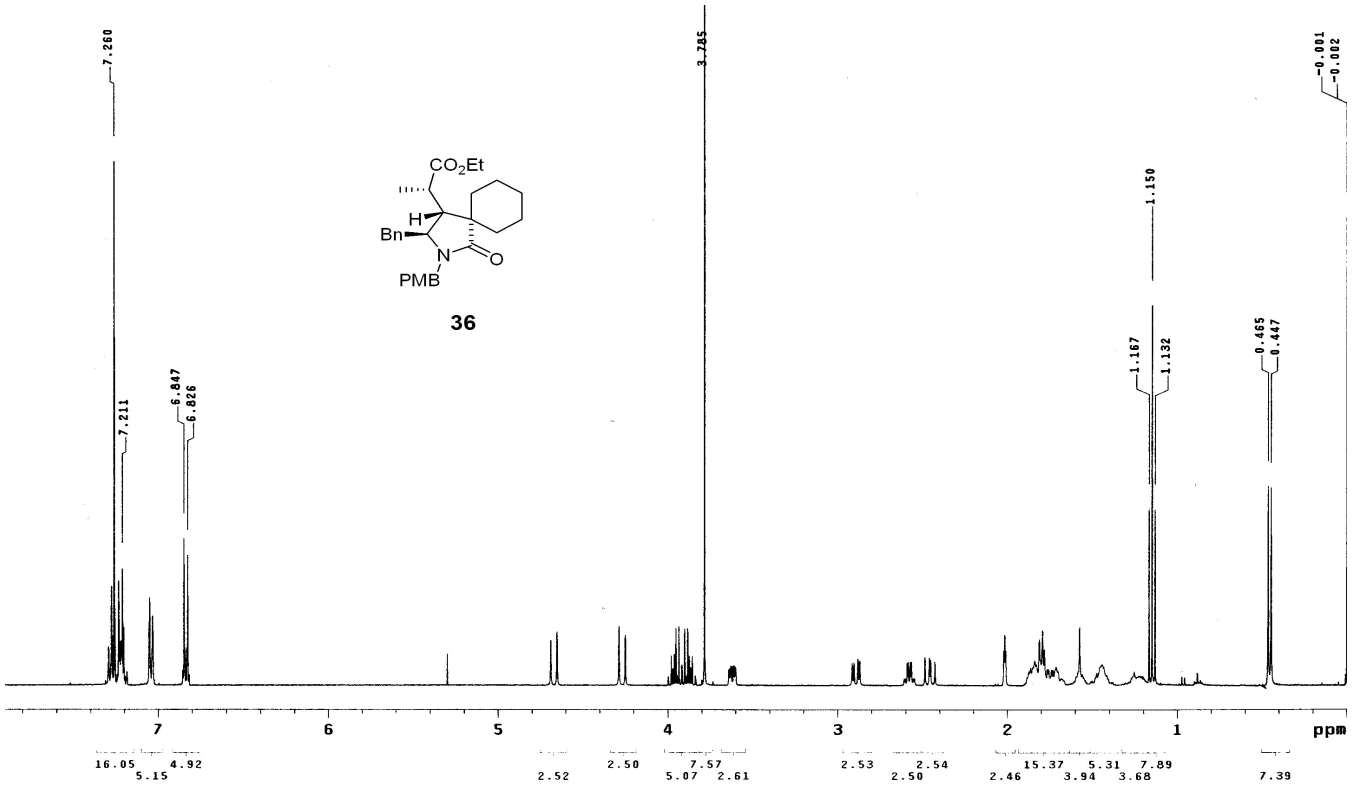


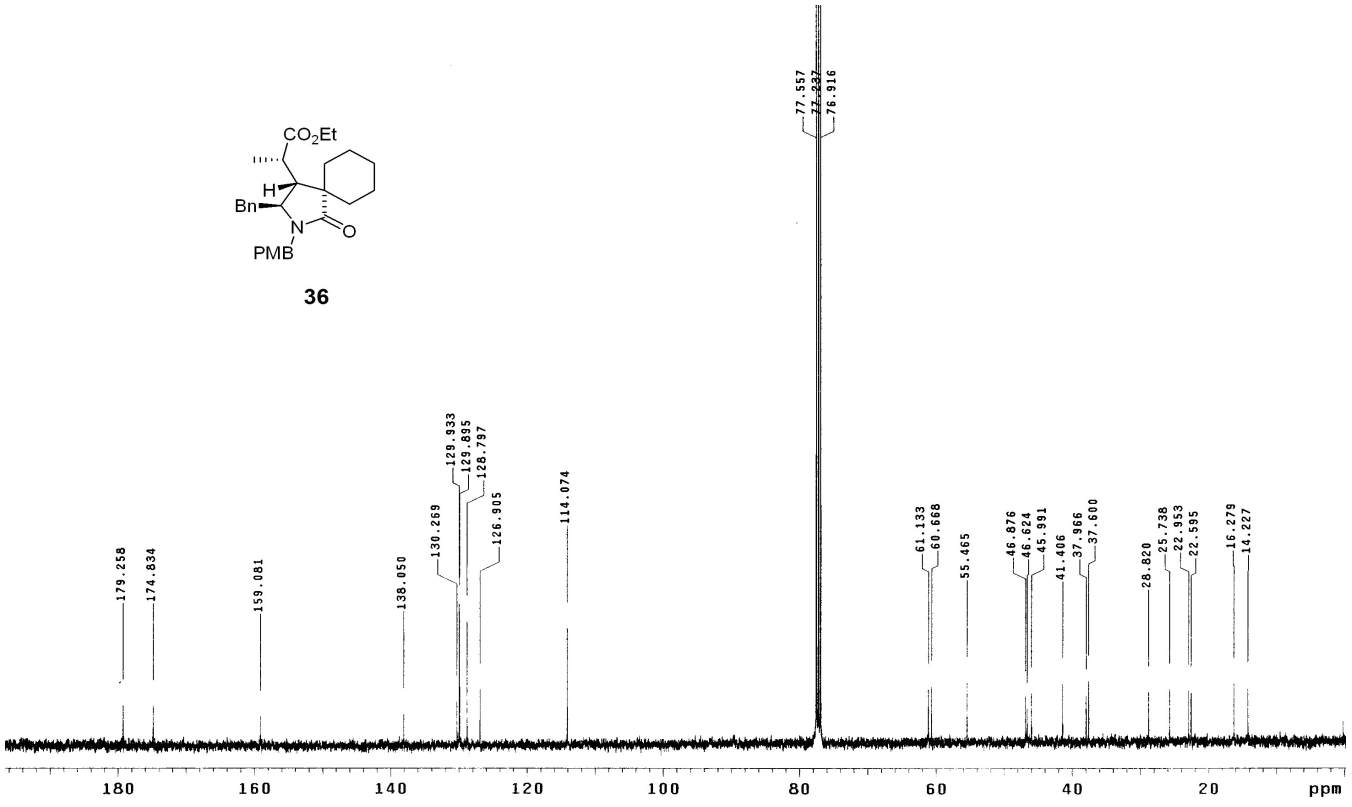

7.261
7.216
7.194
7.048
6.858
6.836
3.794
1.162
1.180
1.144
0.568
0.551
CO2Et
H
Bn
N
PMB
O
29b
7
6
5
4
3
2
1
ppm
18.99
5.97
5.75
2.80
5.62
2.80
2.87
2.88
5.88
8.89
2.94
5.78
5.79
2.94
2.91
8.74
8.46

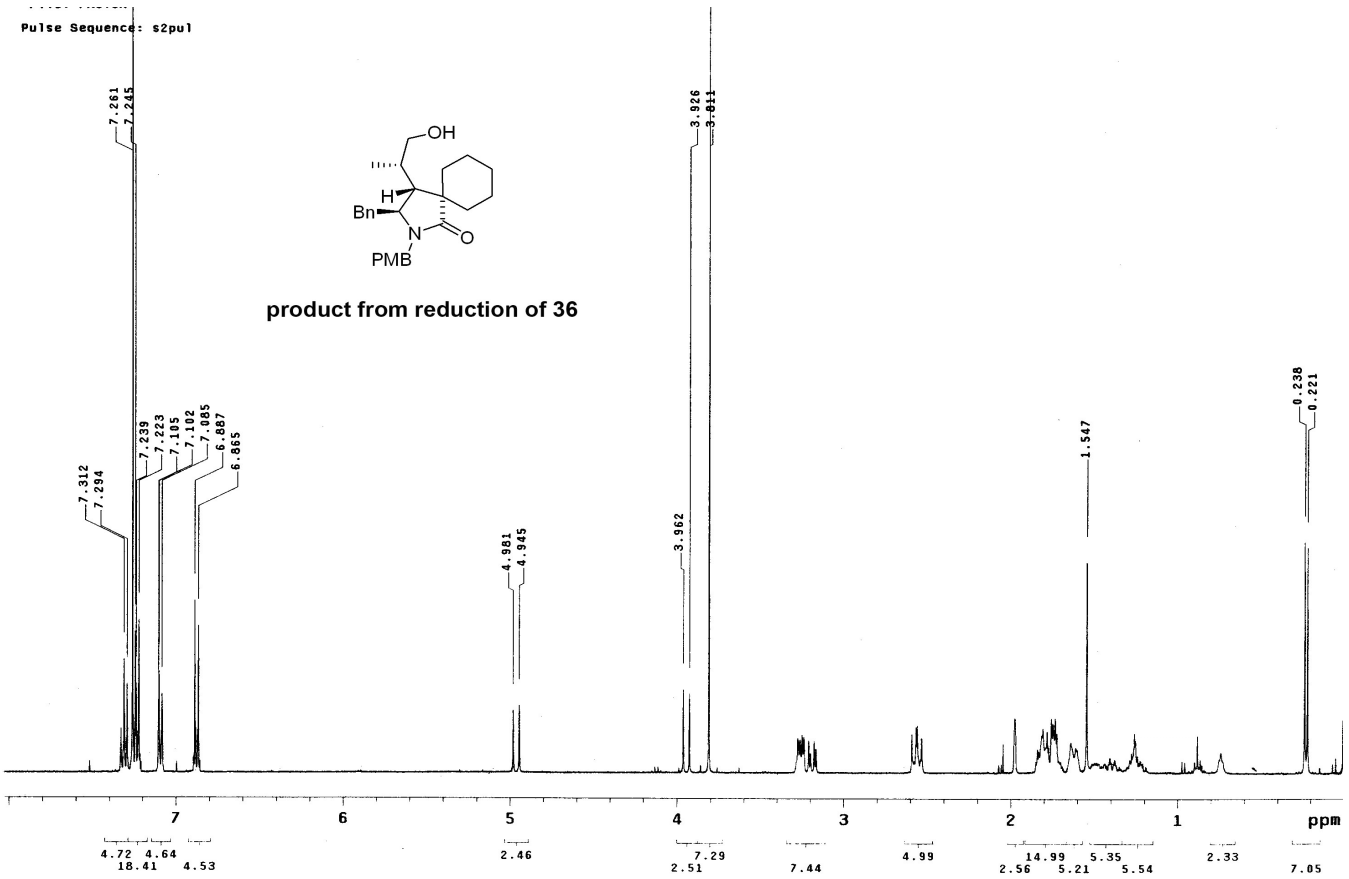

CO2Et
H
Bn
N
PMB
O
29b
gCOSY
F2 (ppm)
F1 (ppm)
1
2
3
4
5
6
7
0

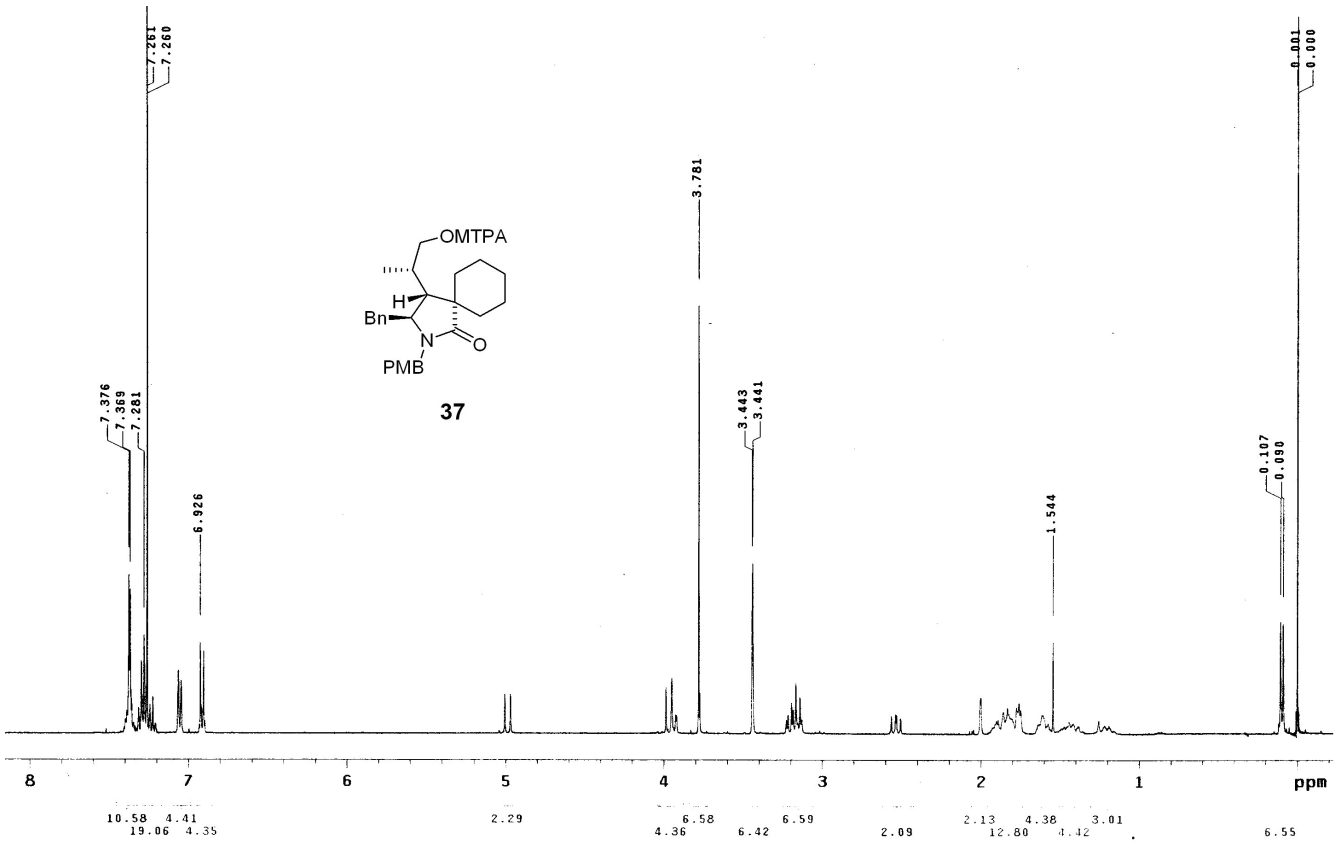

CO2Et
S
H
S
Bn
S
N
O
PMB
29b
77.557
77.237
76.916
130.101
129.834
129.643
128.774
126.905
137.783
131.245
126.348
124.189
123.998
114.166
177.626
174.590
159.241
60.782
60.729
55.473
51.285
47.509
46.121
41.994
41.010
26.524
16.141
14.211
180
160
140
120
100
80
60
40
20
ppm

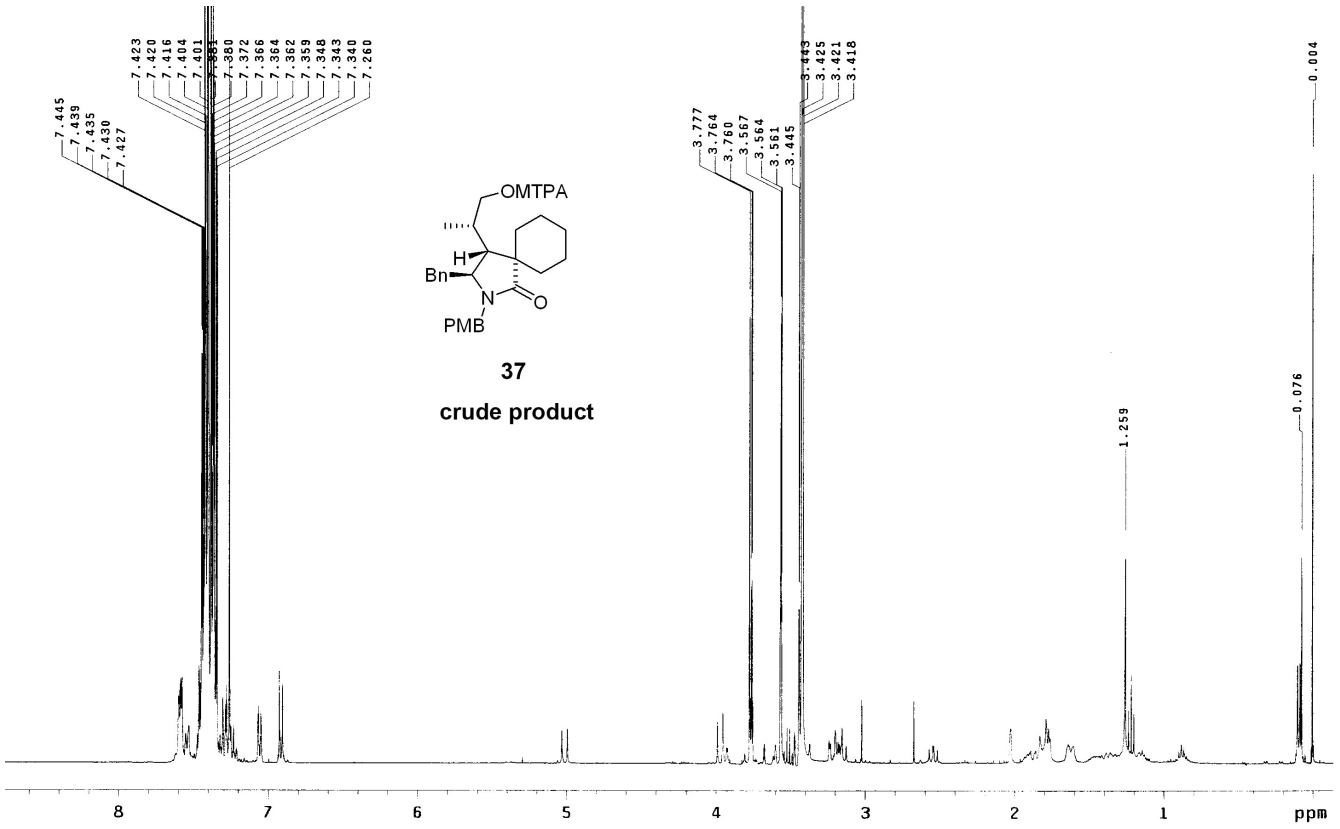

CO2Et
S
H
S
Bn
S
N
O
PMB
29b
NOESY
F2 (ppm)
1
2
3
4
5
6
7
7
6
5
4
3
2
1
0
F1 (ppm)


7.260
7.211
6.847
6.826
3.785
1.150
1.167
1.132
0.465
0.447
-0.001
-0.002
CO2Et
H
Bn
N
O
PMB
36
7
6
5
4
3
2
1
ppm
16.05
5.15
4.92
2.52
2.50
7.57
5.07
2.61
2.53
2.54
2.50
15.37
2.46
5.31
3.94
7.89
3.68
7.39


77.557
77.237
76.916
179.258
174.834
159.081
138.050
130.269
129.933
129.895
128.797
126.905
114.074
61.133
60.668
55.465
46.876
46.624
45.991
41.406
37.966
37.600
28.820
25.738
22.953
22.595
16.279
14.227
CO2Et
H
Bn
N
O
PMB
36
180
160
140
120
100
80
60
40
20
ppm

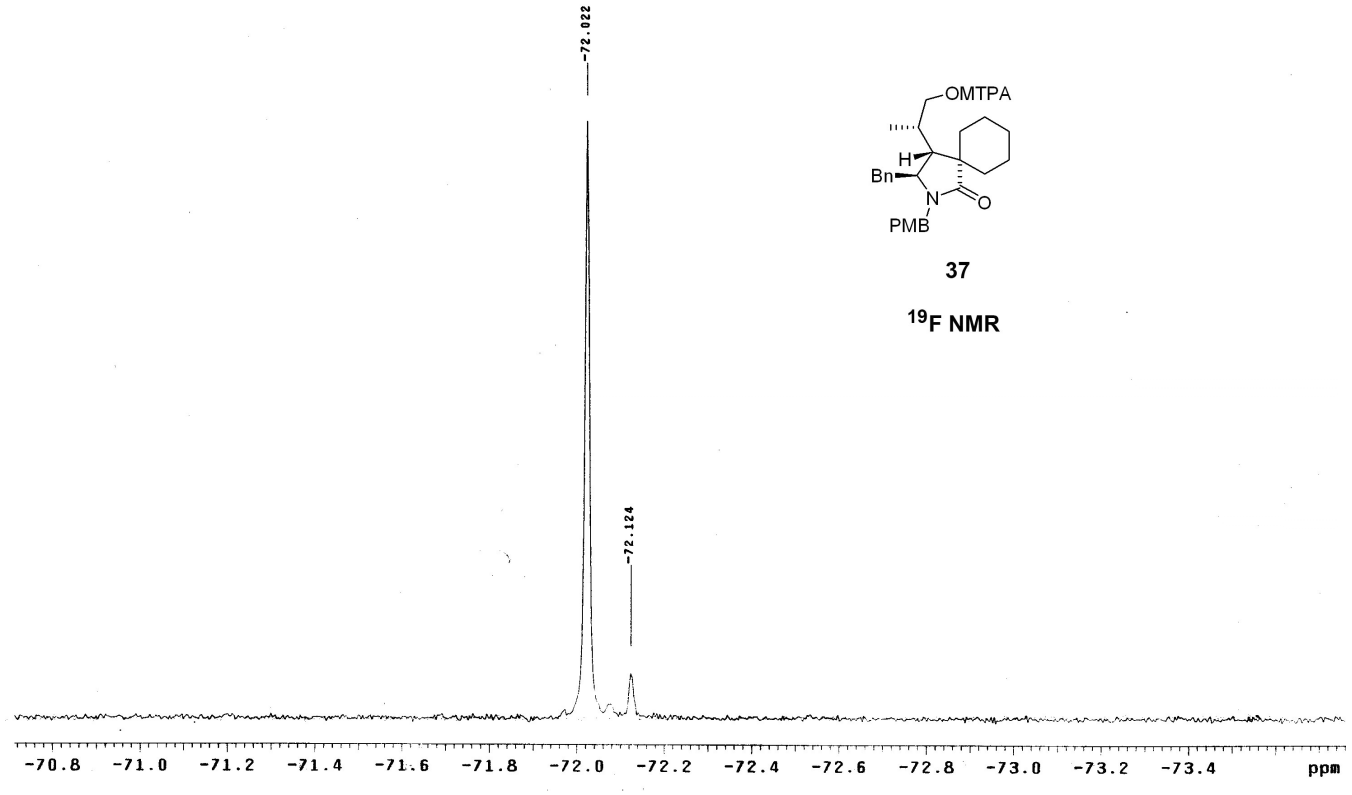

Pulse Sequence: s2pul
OH
H
Bn
N
O
PMB
product from reduction of 36
7.261
7.245
3.926
3.911
7.312
7.294
7.239
7.223
7.105
7.102
7.085
6.887
6.865
4.981
4.945
3.962
1.547
0.238
0.221
ppm


OMTPA
H
Bn
N
O
PMB
37
7.261
7.260
3.781
0.001
0.000
7.376
7.369
7.281
6.926
3.443
3.441
0.107
0.090
1.544
ppm



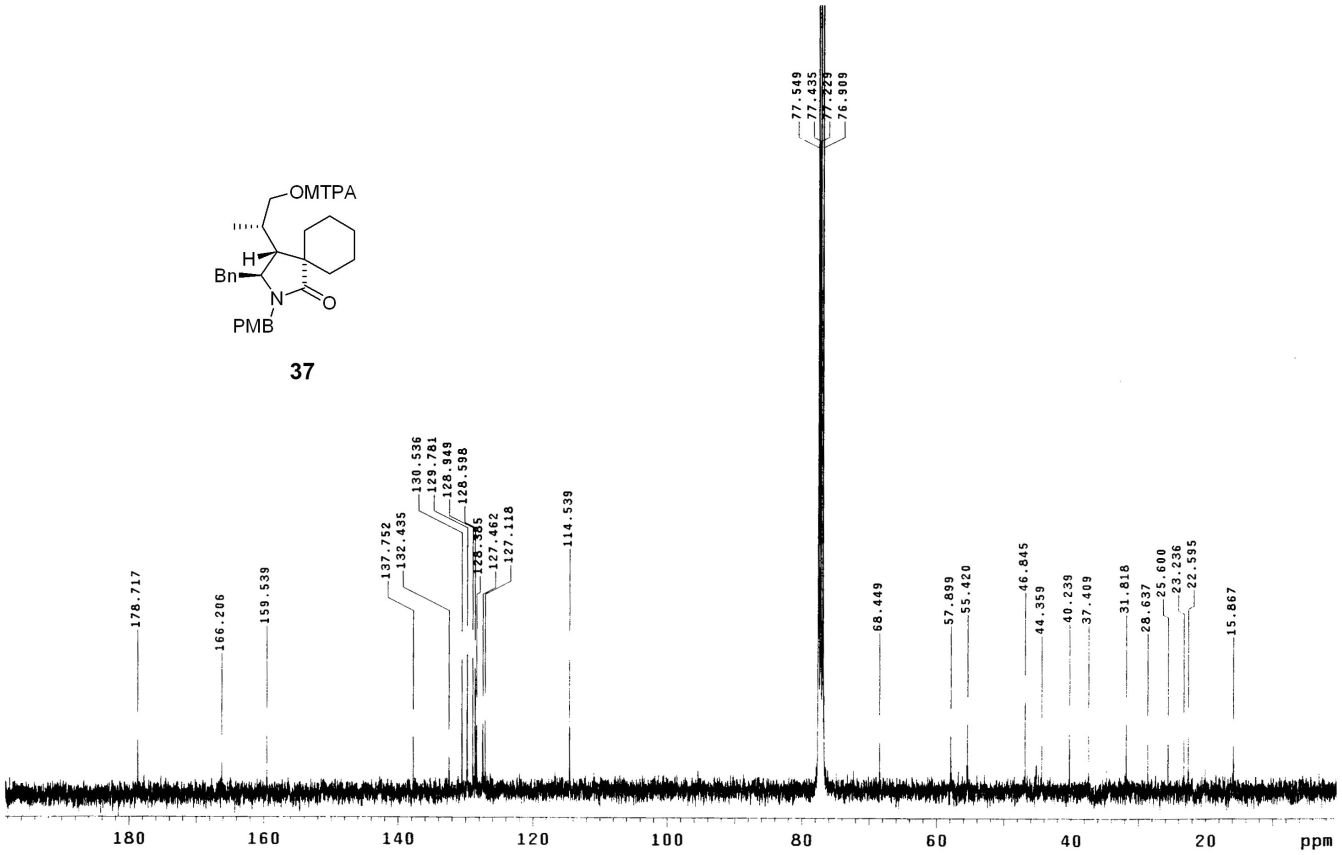
37

crude product

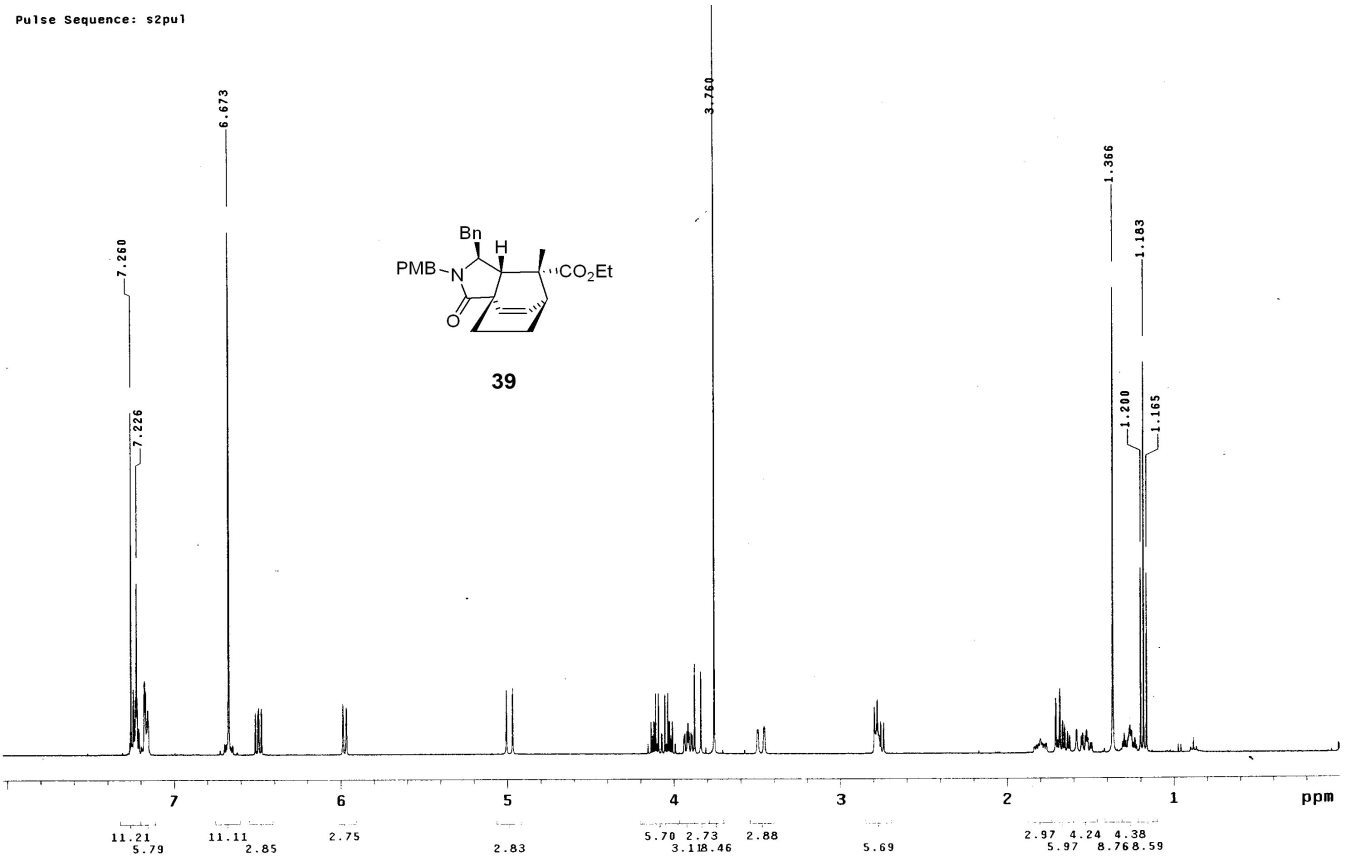


37

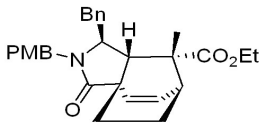
^{19}F NMR


OMTPA
H
Bn
N
O
PMB
77.549
77.435
77.229
76.909
178.717
166.206
159.539
137.752
132.435
130.536
129.781
128.949
128.598
128.385
127.462
127.118
114.539
68.449
57.899
55.420
46.845
44.359
40.239
37.409
31.818
28.637
25.600
23.236
22.595
15.867
180
160
140
120
100
80
60
40
20
ppm

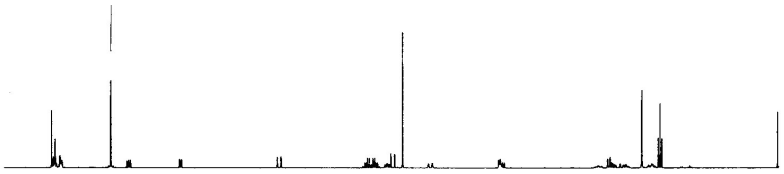
37


Pulse Sequence: s2pul
Bn
H
PMB
N
O
CO2Et
7.260
7.226
6.673
3.760
1.366
1.183
1.200
1.165
7
6
5
4
3
2
1
ppm
11.21
5.79
11.11
2.85
2.75
2.83
5.70
2.73
3.11
8.46
2.88
5.69
2.97
4.24
4.38
5.97
8.76
8.59

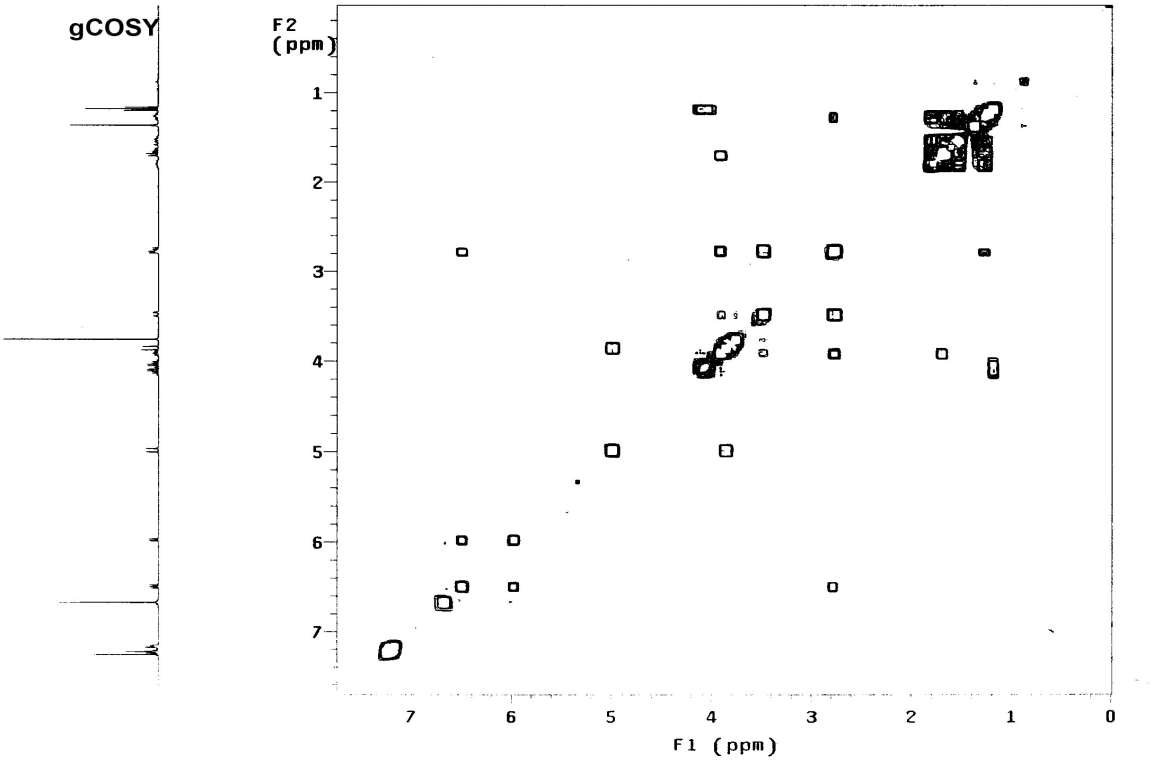
39

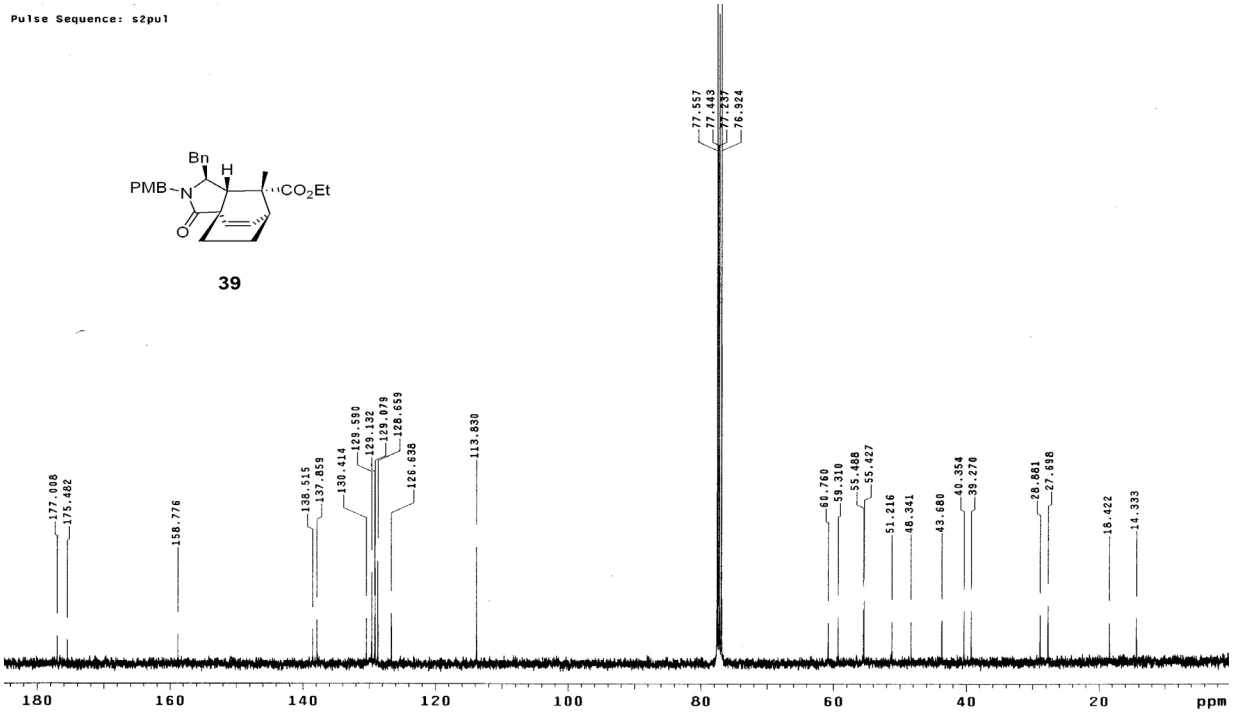

Bn
H
PMB
N
O
CO2Et

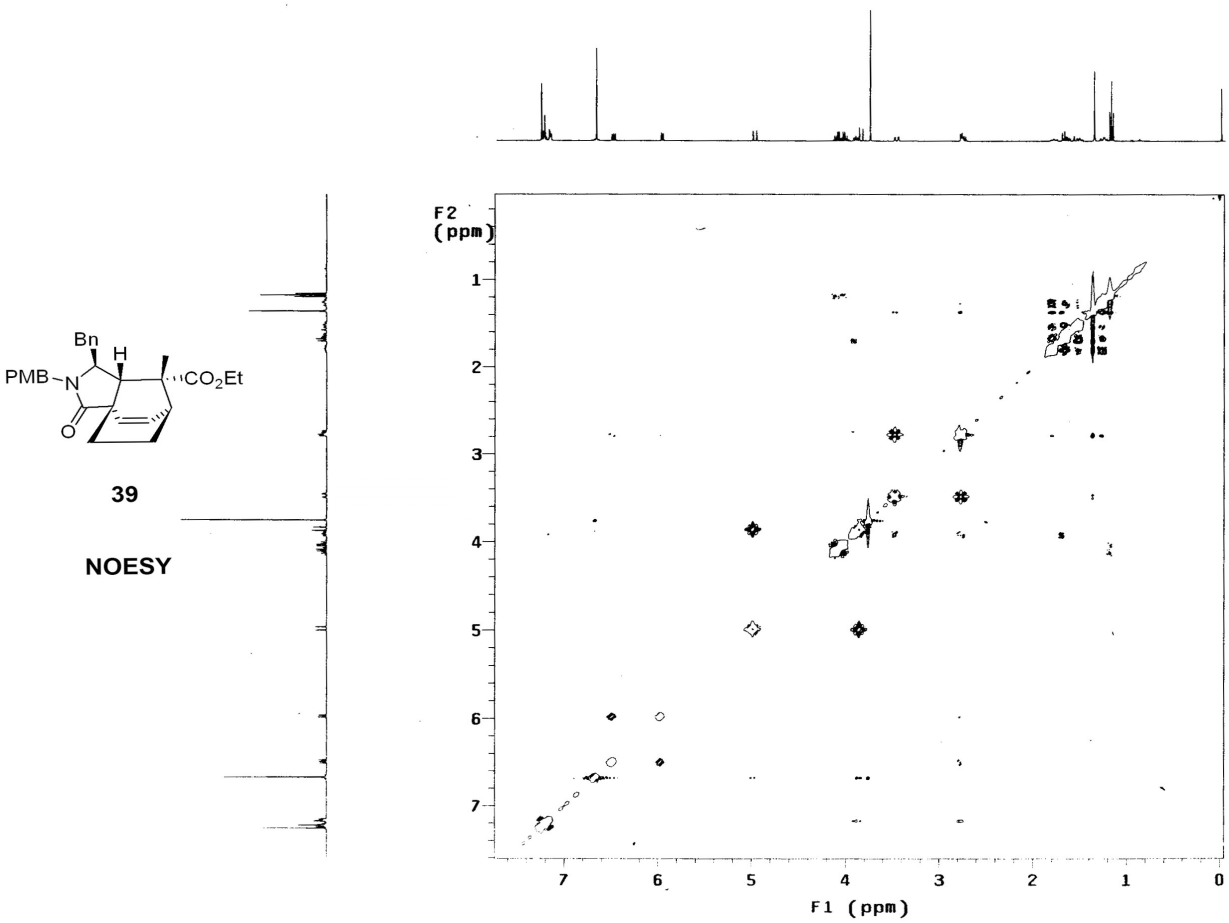
39

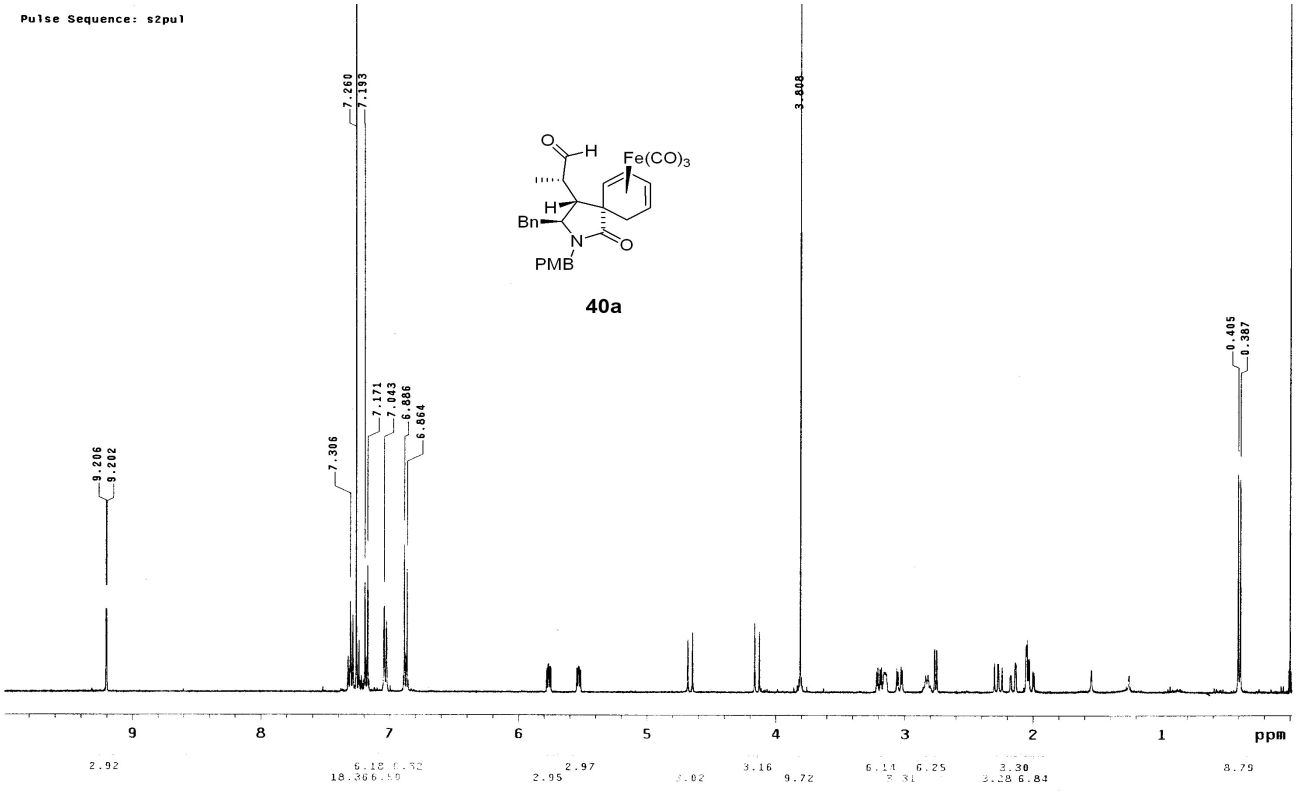


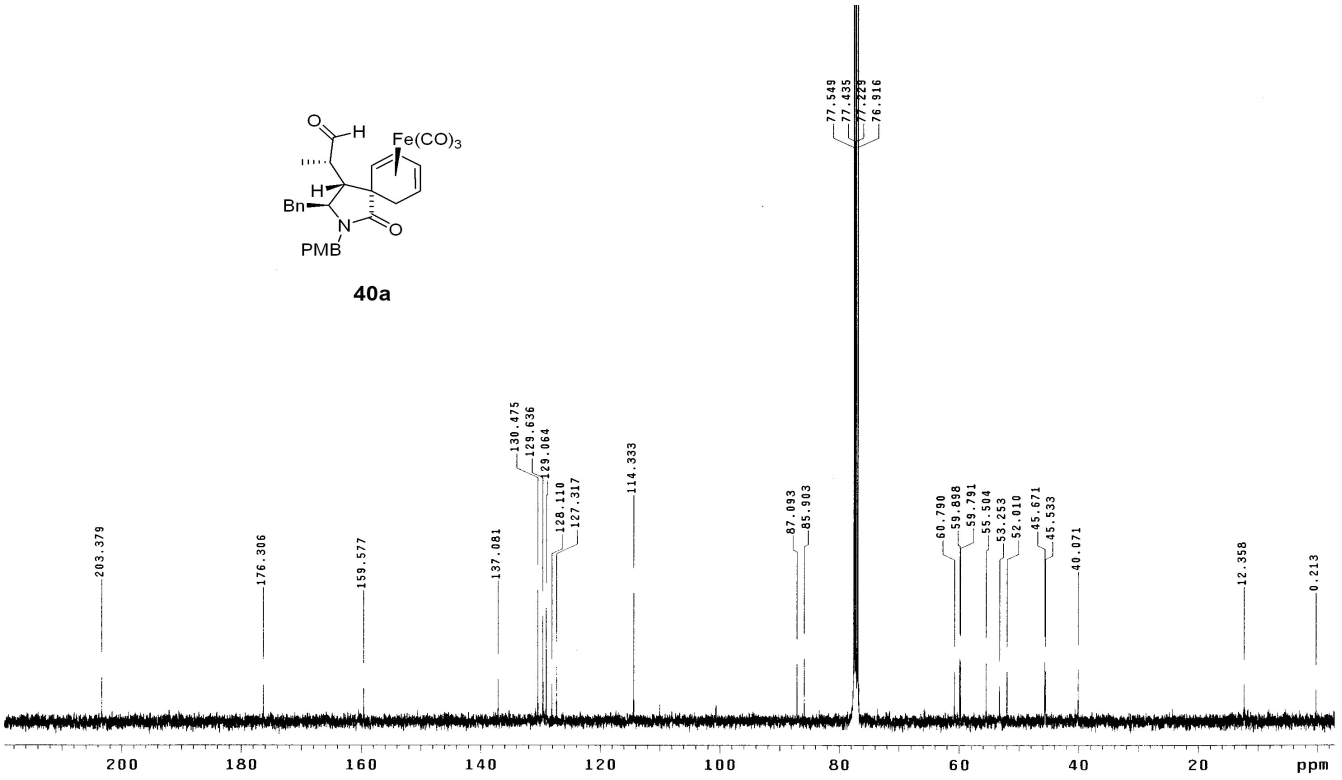
gCOSY

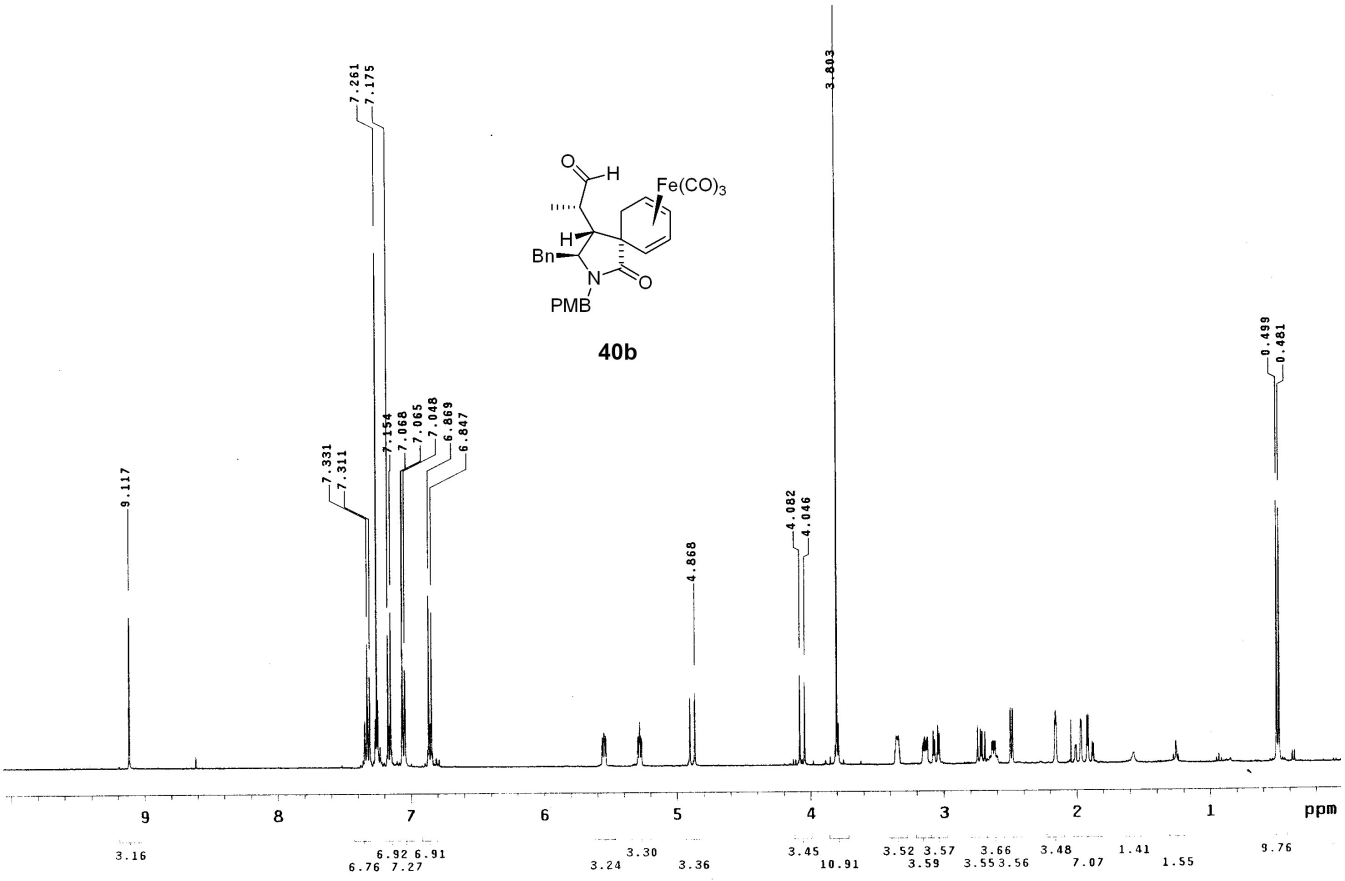

F2 (ppm)
F1 (ppm)

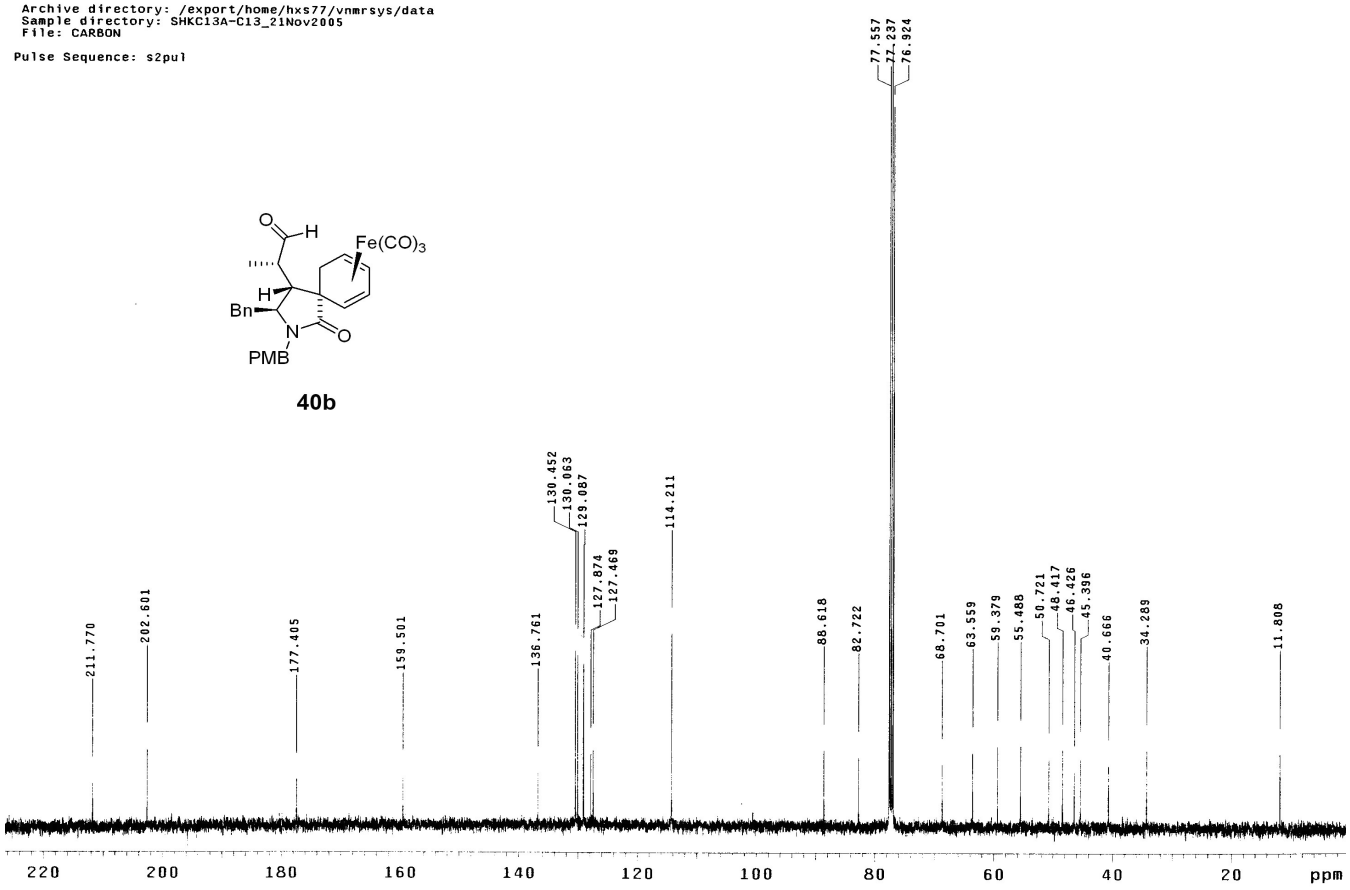

Pulse Sequence: s2pul
Bn
H
PMB
N
O
CO2Et
39
177.008
175.462
158.776
138.515
137.859
130.414
129.590
129.132
129.079
128.659
126.638
113.830
77.557
77.443
77.237
76.924
60.760
59.310
55.488
55.427
51.216
48.341
43.680
40.354
39.270
28.861
27.698
18.422
14.333
ppm


Bn
H
PMB
N
O
CO2Et
39
NOESY
F2 (ppm)
F1 (ppm)


Pulse Sequence: s2pul
9.206
9.202
7.306
7.260
7.193
7.171
7.043
6.886
6.864
3.808
0.405
0.387
O
H
Fe(CO)3
Bn
N
PMB
40a
ppm

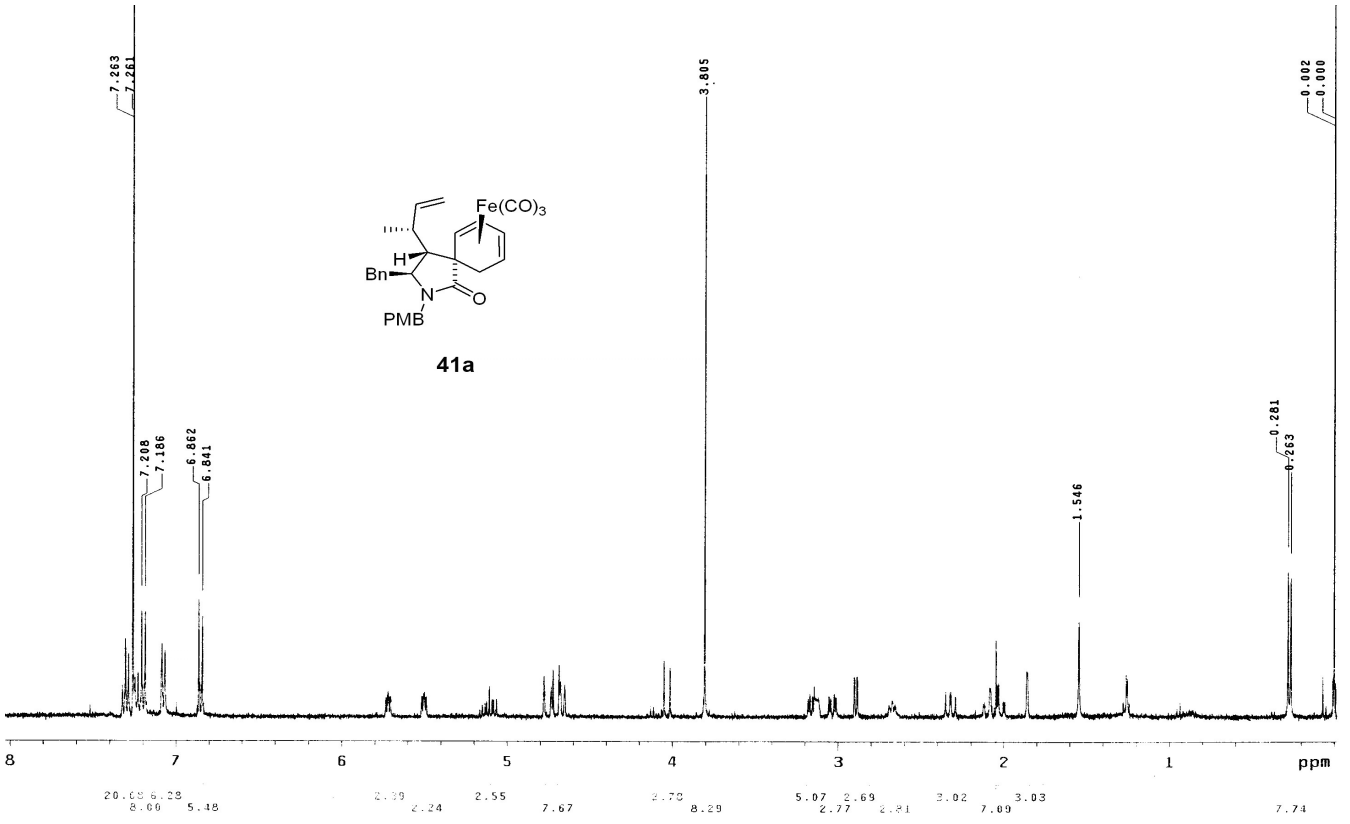

O
H
Fe(CO)3
H
Bn
N
O
PMB
40a
77.549
77.435
77.225
76.916
130.475
129.636
129.064
128.110
127.317
114.333
87.093
85.903
60.790
59.898
59.791
55.504
53.253
52.010
45.671
45.533
40.071
12.358
0.213
203.379
176.306
159.577
137.081
200
180
160
140
120
100
80
60
40
20
ppm


O
H
Fe(CO)3
H
Bn
N
O
PMB
40b
7.261
7.175
3.803
0.499
0.481
9.117
7.331
7.311
7.154
7.068
7.065
7.048
6.869
6.847
4.868
4.082
4.046
9
8
7
6
5
4
3
2
1
ppm
3.16
6.92 6.91
6.76 7.27
3.24
3.30
3.36
3.45
10.91
3.52 3.57
3.59
3.55 3.66
3.56
3.48
7.07
1.41
1.55
9.76


Archive directory: /export/home/hxs77/vnmrsys/data
Sample directory: SHKC13A-C13_21Nov2005
File: CARBON
Pulse Sequence: s2pul
77.557
77.237
76.924
130.452
130.063
129.087
114.211
127.874
127.469
211.770
202.601
177.405
159.501
136.761
88.618
82.722
68.701
63.559
59.379
55.488
50.721
48.417
46.426
45.396
40.666
34.289
11.808
220
200
180
160
140
120
100
80
60
40
20
ppm

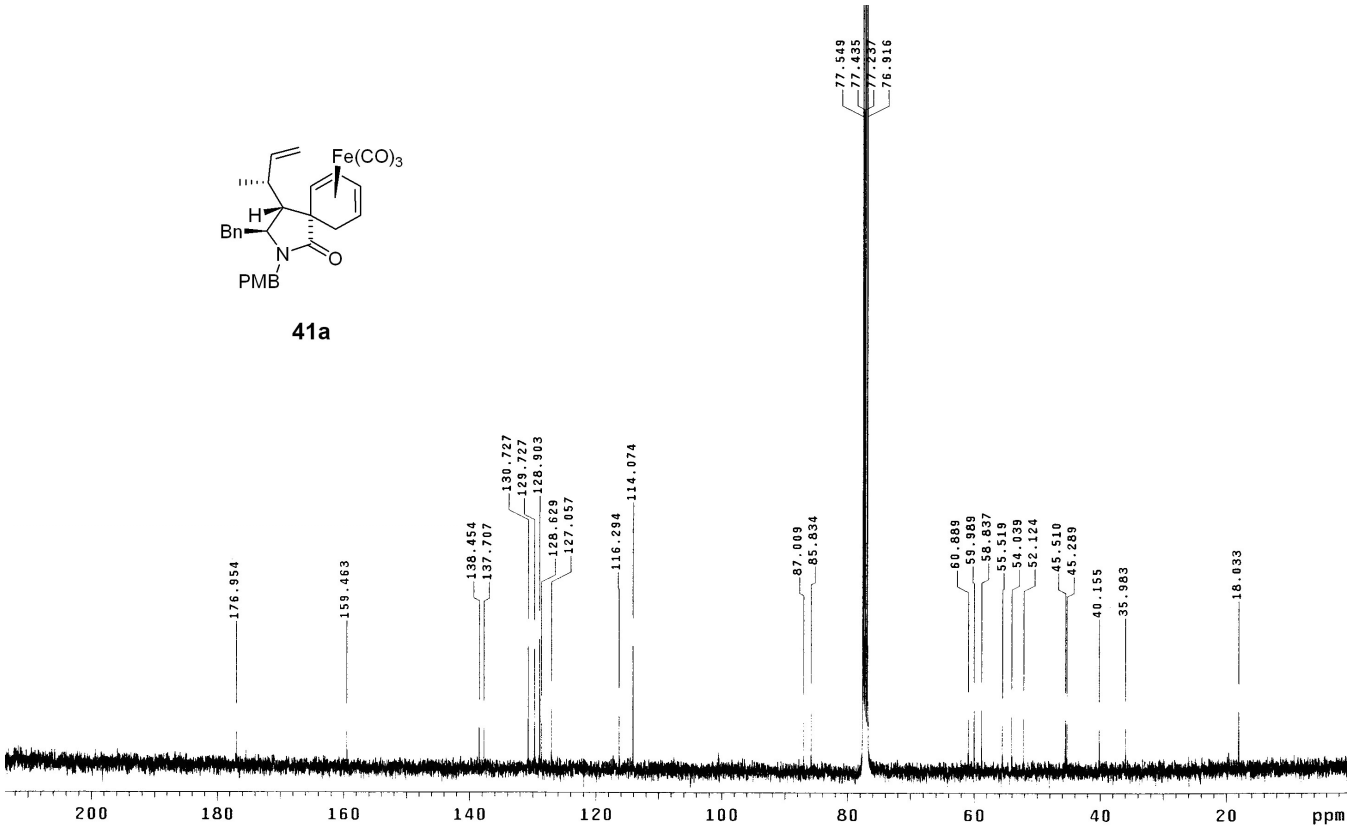
O
H
Fe(CO)3
H
Bn
N
O
PMB

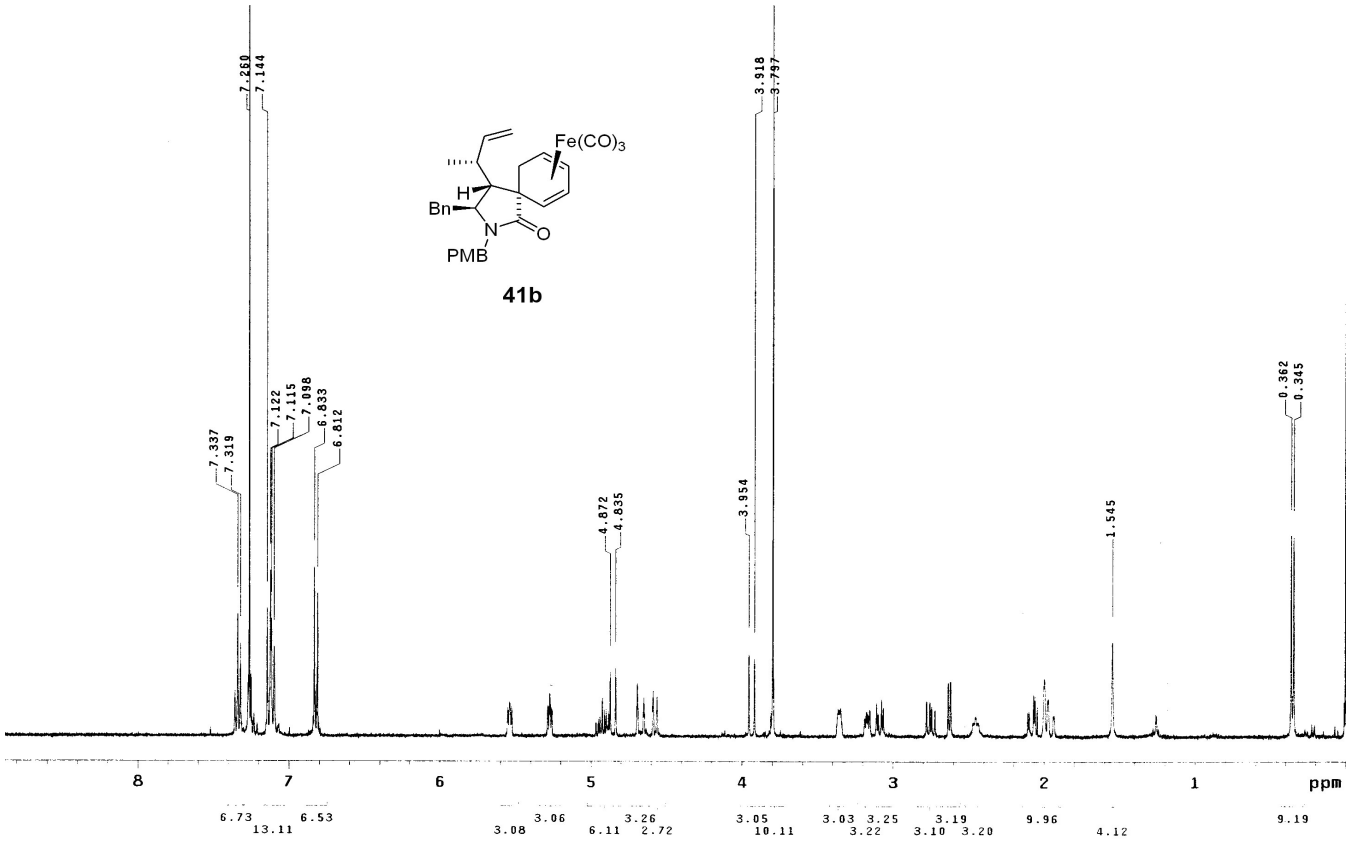
40b

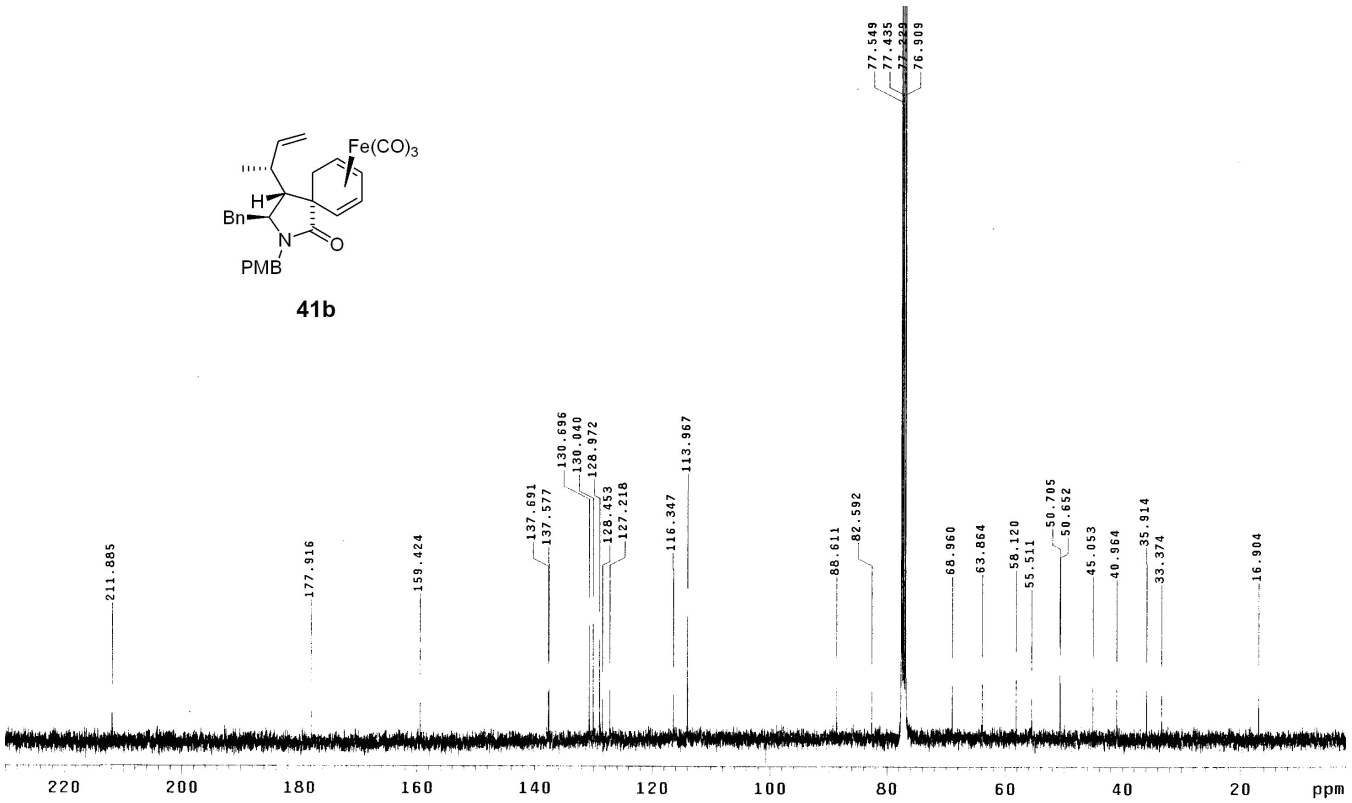

7.263
7.261
3.805
0.002
0.000
7.208
7.186
6.862
6.841
1.546
0.281
0.263
8
7
6
5
4
3
2
1
ppm
20.00 6.28
8.00 5.48
2.39
2.24
2.55
7.67
2.70
8.29
5.07 2.69
2.77 2.81
3.02
7.09
3.03
7.74

Fe(CO)3
H
Bn
N
O
PMB

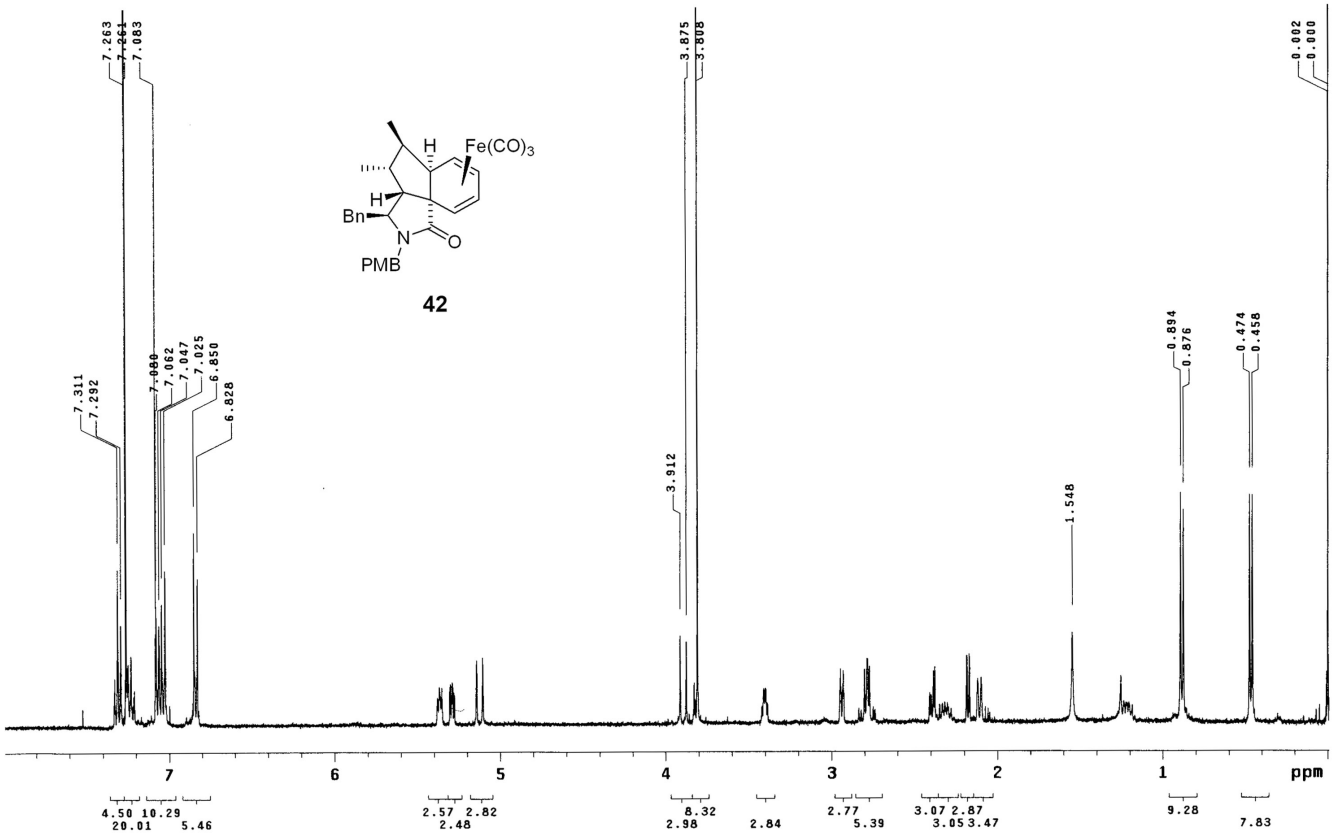
41a


Fe(CO)3
H
Bn
N
O
PMB
41a
176.954
159.463
138.454
137.707
130.727
129.727
128.903
128.629
127.057
116.294
114.074
87.009
85.834
77.549
77.435
77.237
76.916
60.889
59.989
58.837
55.519
54.039
52.124
45.510
45.289
40.155
35.983
18.033
200
180
160
140
120
100
80
60
40
20
ppm

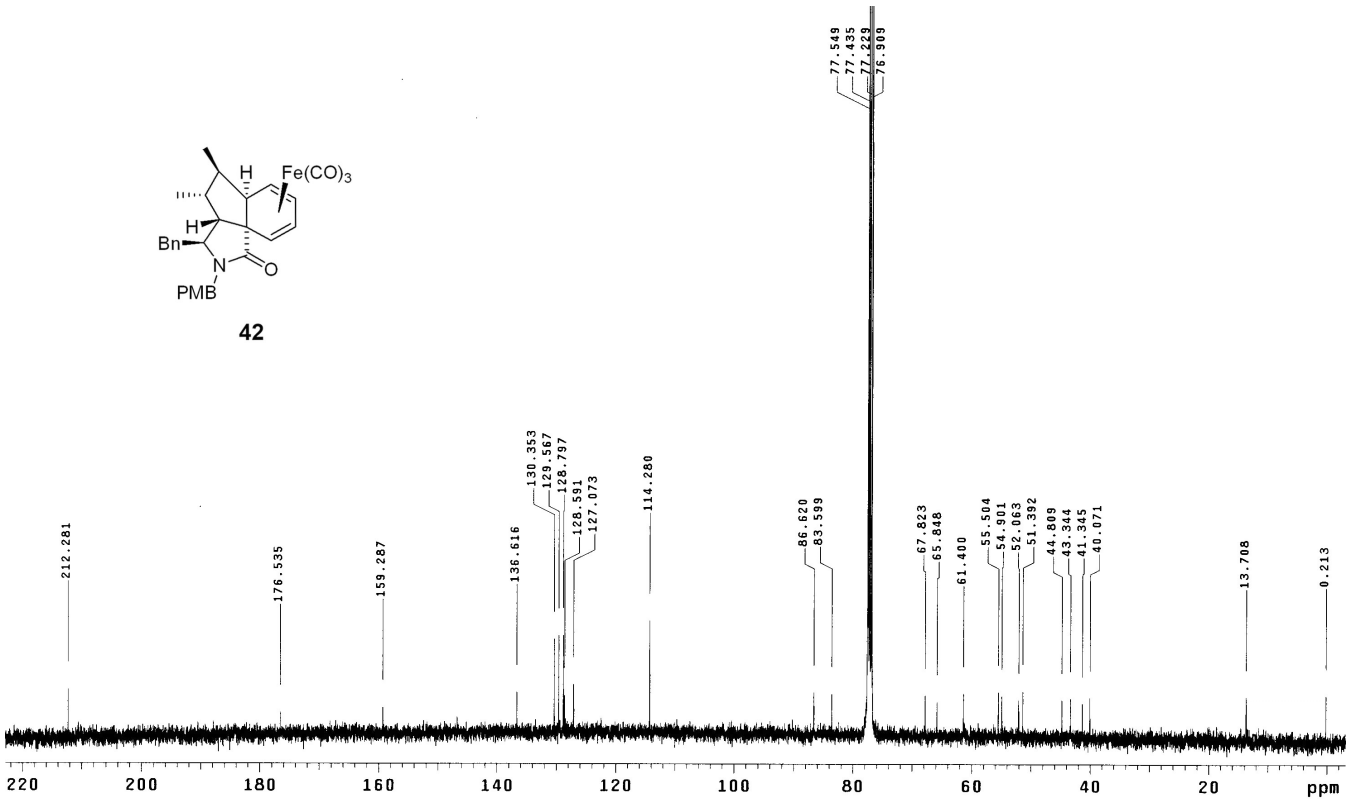

Fe(CO)3
H
Bn
N
O
PMB
41b
7.260
7.144
7.337
7.319
7.122
7.115
7.098
6.833
6.812
4.872
4.835
3.954
3.918
3.797
1.545
0.362
0.345
8
7
6
5
4
3
2
1
ppm
6.73
13.11
6.53
3.08
3.06
6.11
3.26
2.72
3.05
10.11
3.03
3.22
3.25
3.10
3.19
3.20
9.96
4.12
9.19


Fe(CO)3
H
Bn
N
O
PMB
77.549
77.435
77.220
76.909
211.885
177.916
159.424
137.691
137.577
130.696
130.040
128.972
128.453
127.218
116.347
113.967
88.611
82.592
68.960
63.864
58.120
55.511
50.705
50.652
45.053
40.964
35.914
33.374
16.904
220
200
180
160
140
120
100
80
60
40
20
ppm

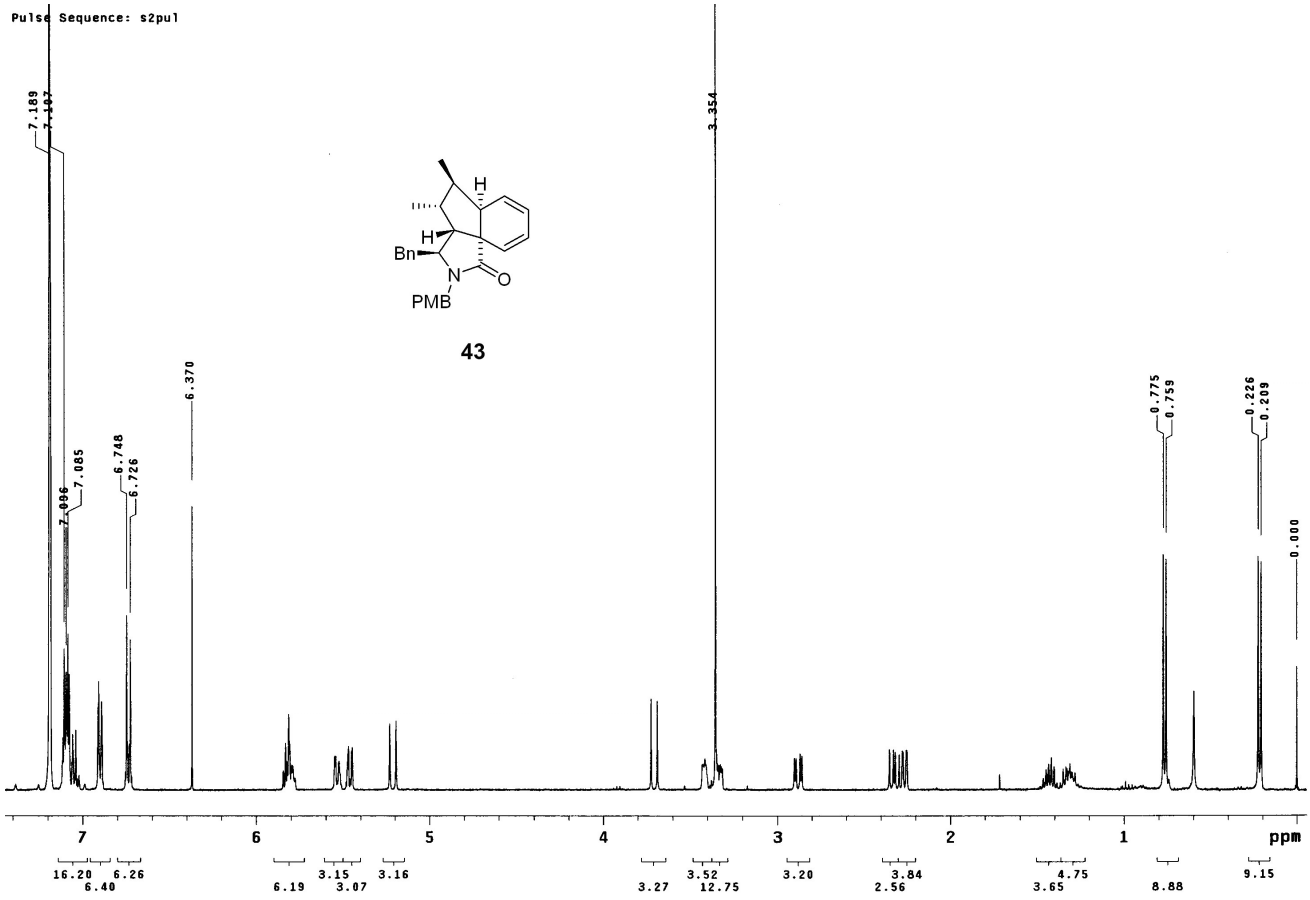
41b


H
Fe(CO)3
H
Bn
N
O
PMB
7.263
7.261
7.083
3.875
3.868
0.002
0.000
7.311
7.292
7.066
7.062
7.047
7.025
6.850
6.828
3.912
1.548
0.894
0.876
0.474
0.458
7
6
5
4
3
2
1
ppm
4.50 10.29
20.01
5.46
2.57 2.82
2.48
8.32
2.98
2.84
2.77
5.39
3.07 2.87
3.05 3.47
9.28
7.83

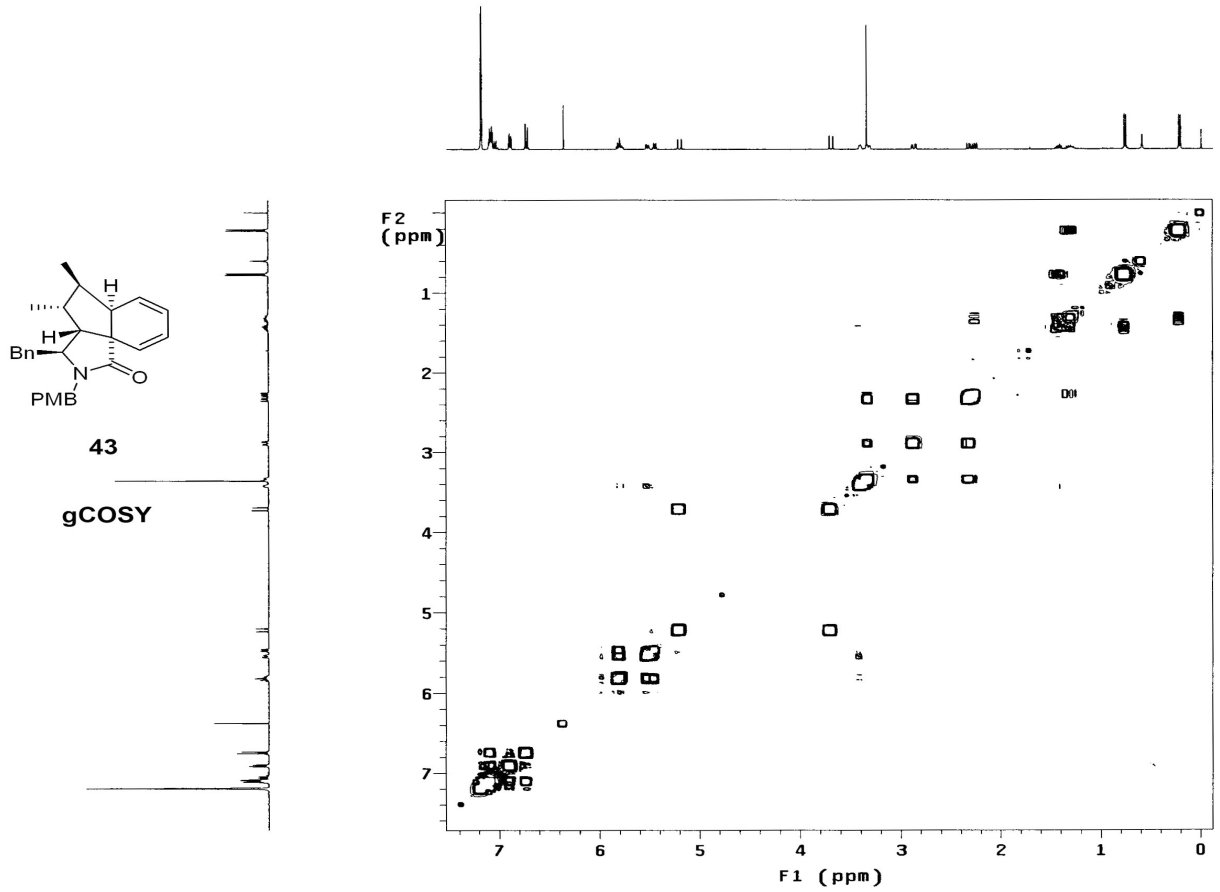
42


H
Fe(CO)3
H
Bn
N
O
PMB
77.549
77.435
77.229
76.909
212.281
176.535
159.287
136.616
130.353
129.567
128.797
128.591
127.073
114.280
86.620
83.599
67.823
65.848
61.400
55.504
54.901
52.063
51.392
44.809
43.344
41.345
40.071
13.708
0.213
220
200
180
160
140
120
100
80
60
40
20
ppm

42

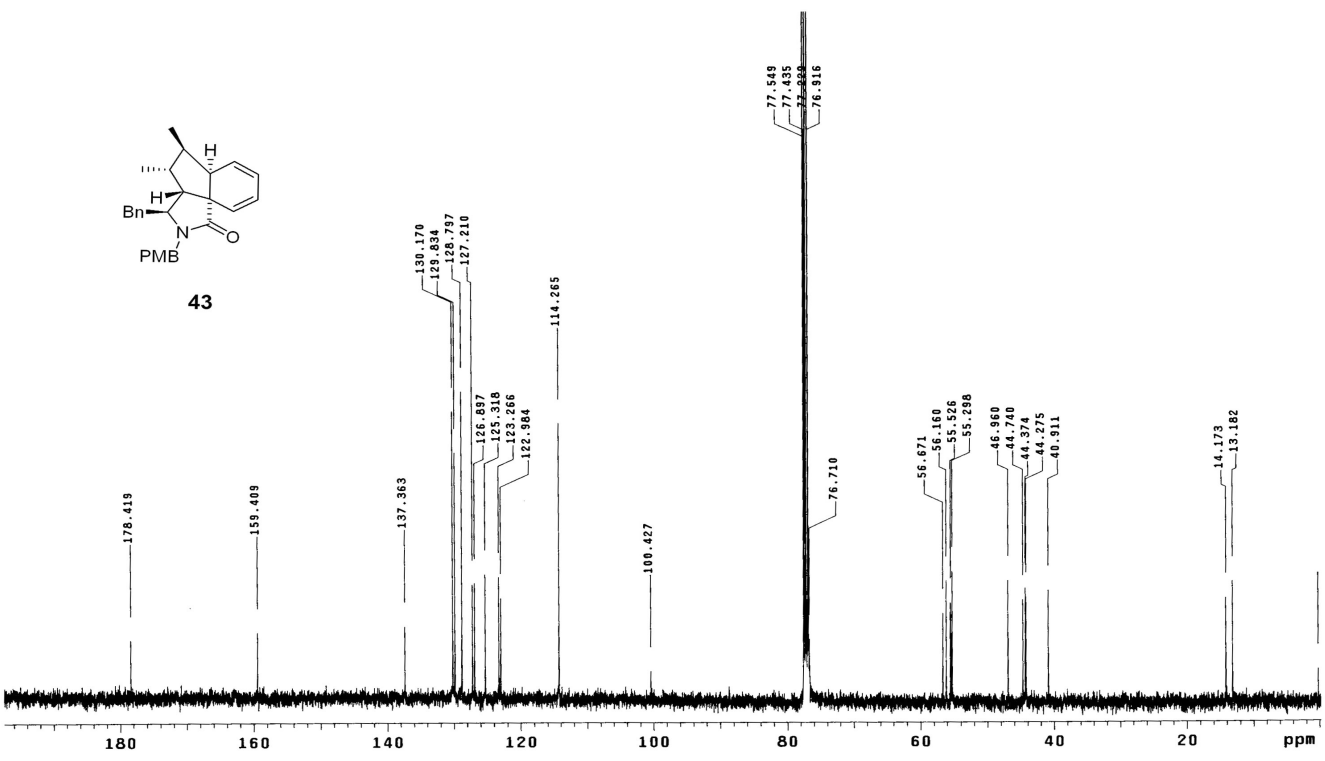

Pulse Sequence: s2pul
7.189
7.107
7.085
7.036
6.748
6.726
6.370
3.354
0.775
0.759
0.226
0.209
0.000
H
H
Bn
N
O
PMB
7
6
5
4
3
2
1
ppm
16.20
6.40
6.26
6.19
3.15
3.07
3.16
3.27
3.52
12.75
3.20
3.84
2.56
4.75
3.65
8.88
9.15

43

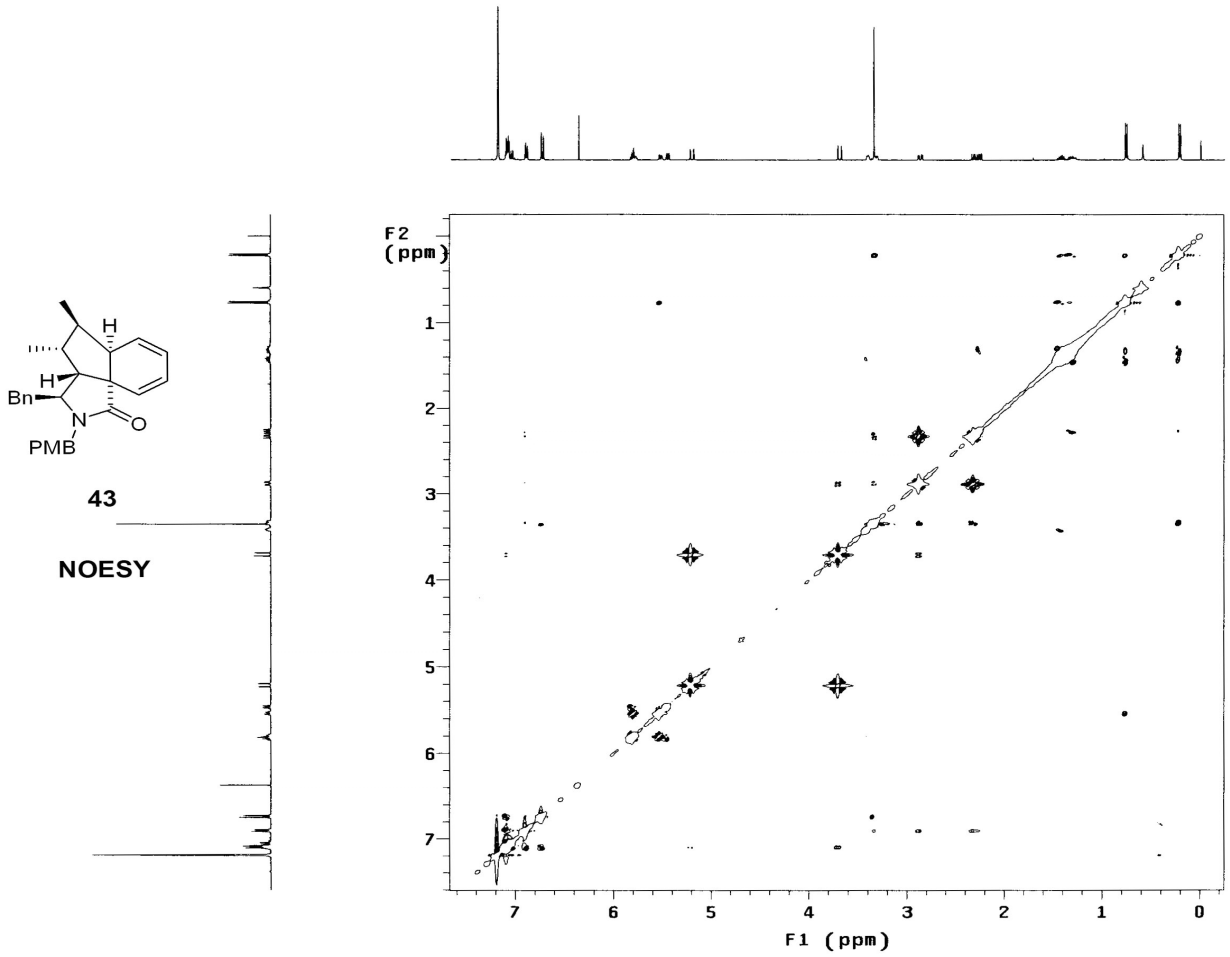

H
H
Bn
N
O
PMB
F2 (ppm)
F1 (ppm)

43

gCOSY

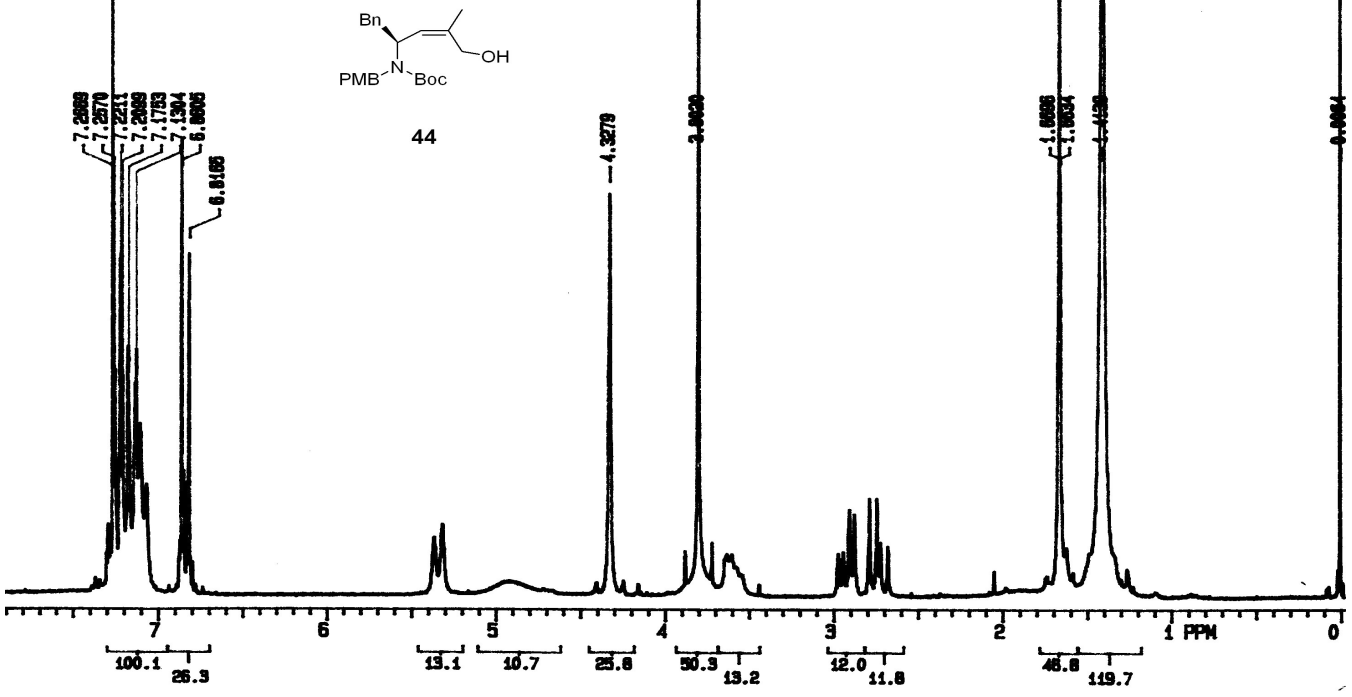

H
H
Bn
N
O
PMB
178.419
159.409
137.363
130.170
129.834
128.797
127.210
126.897
125.318
123.266
122.984
114.265
100.427
77.549
77.435
76.916
76.710
56.671
56.160
55.526
55.298
46.960
44.740
44.374
44.275
40.911
14.173
13.182
ppm

43

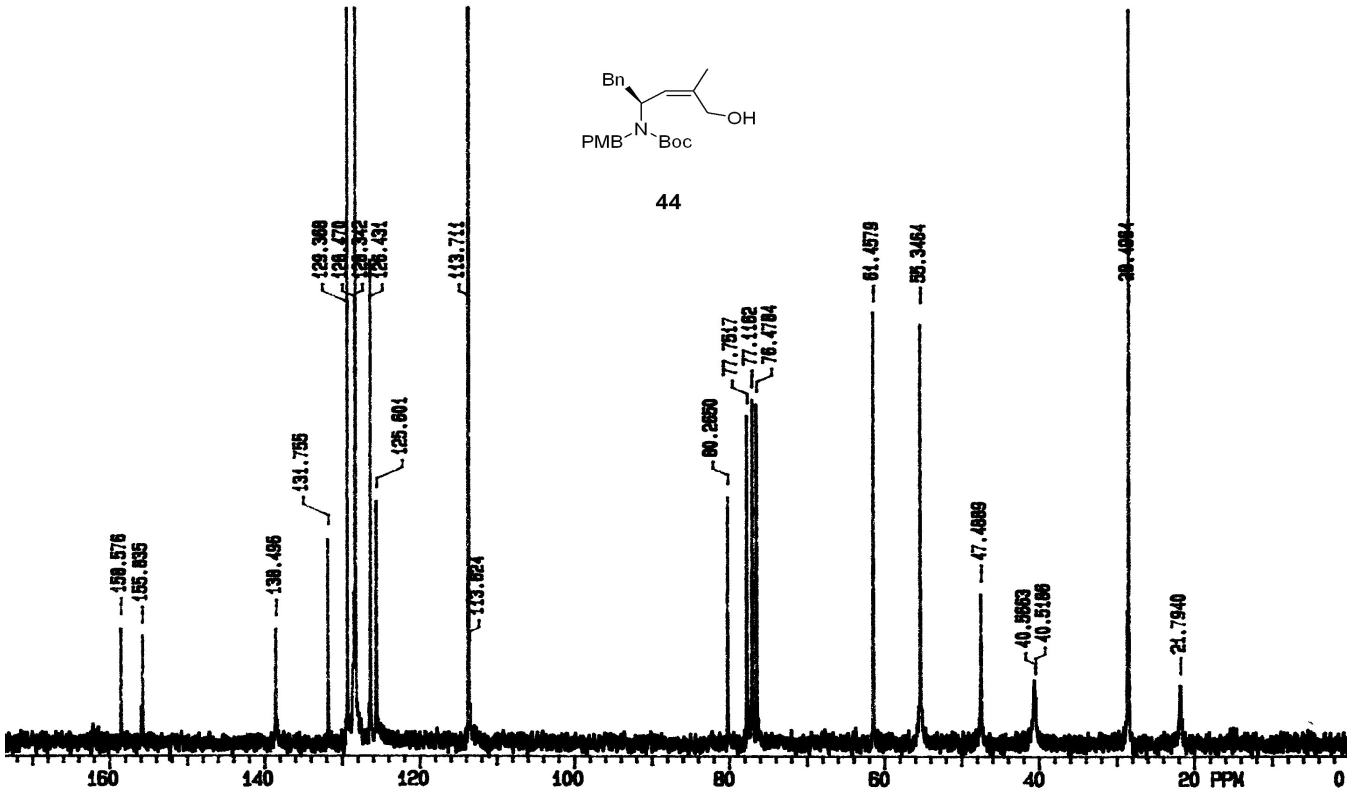

H
H
Bn
N
O
PMB
F2 (ppm)
F1 (ppm)

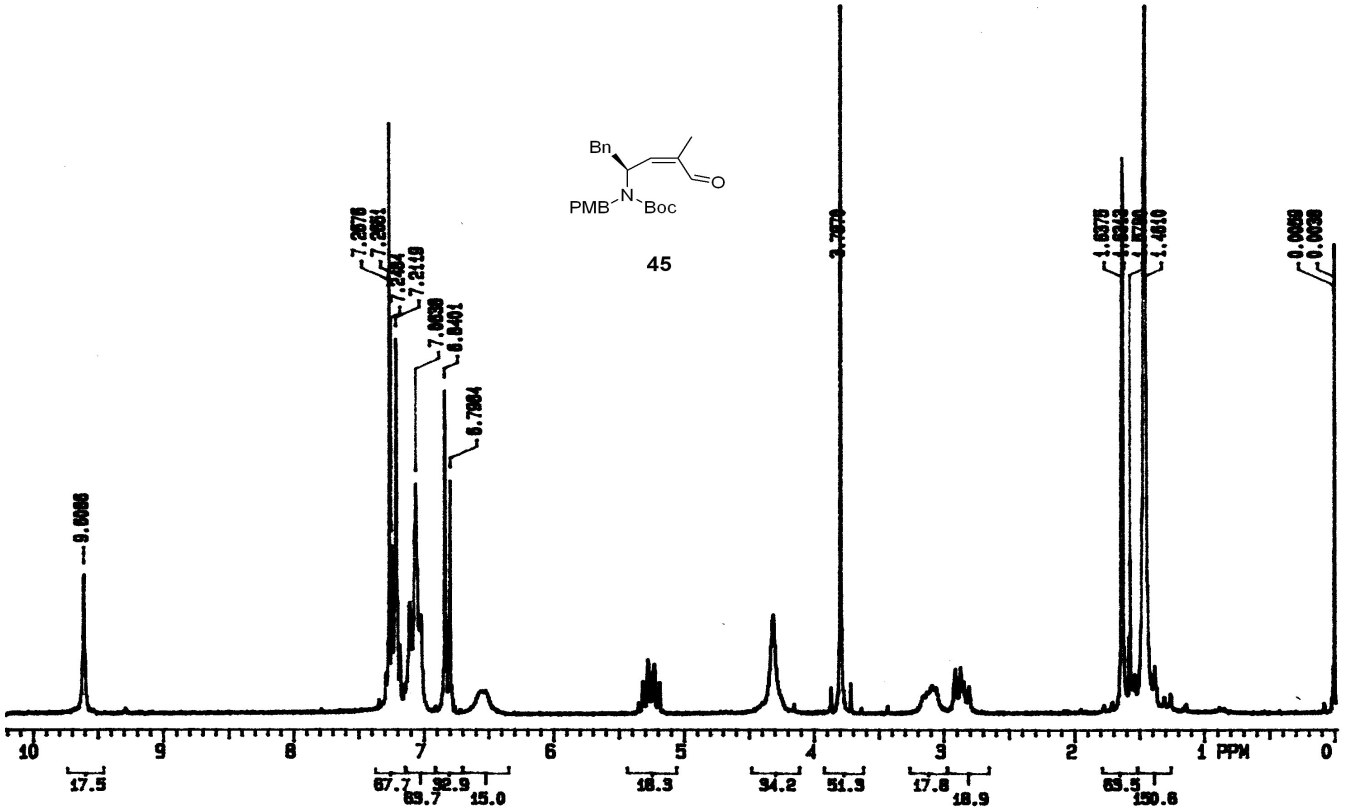
43

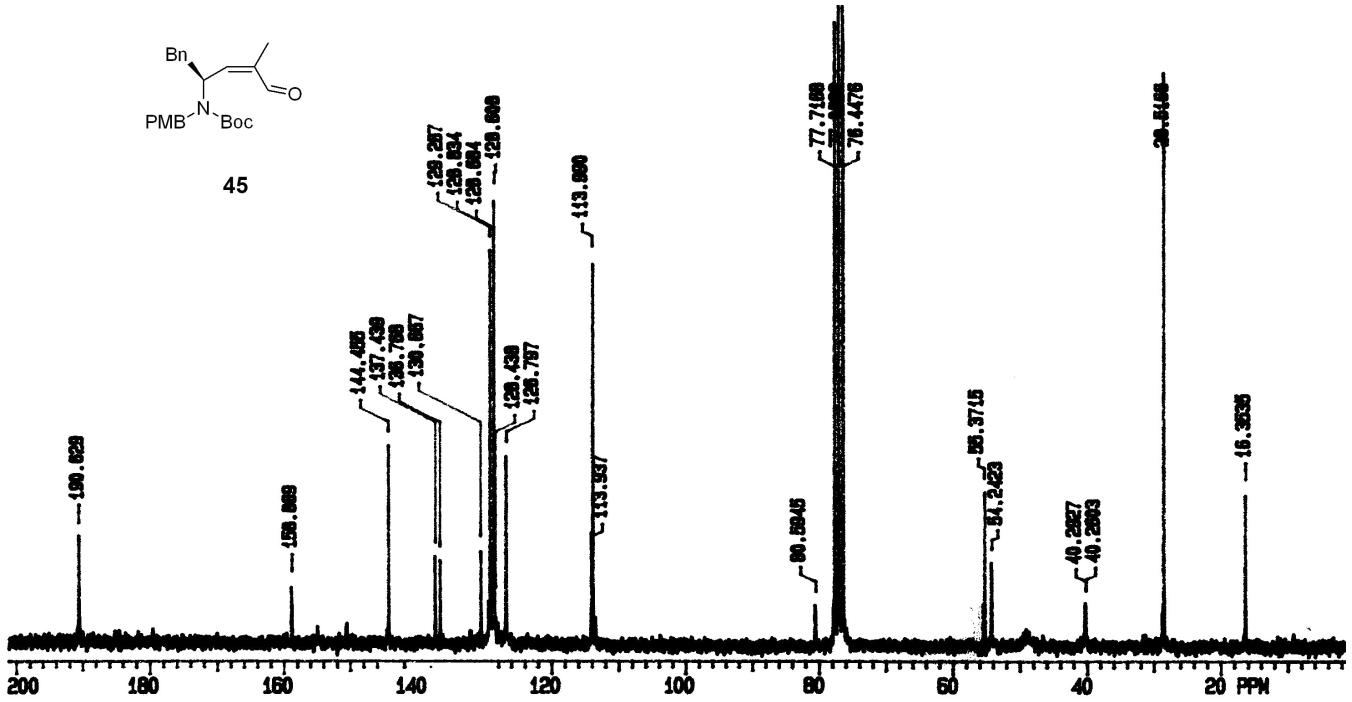
NOESY

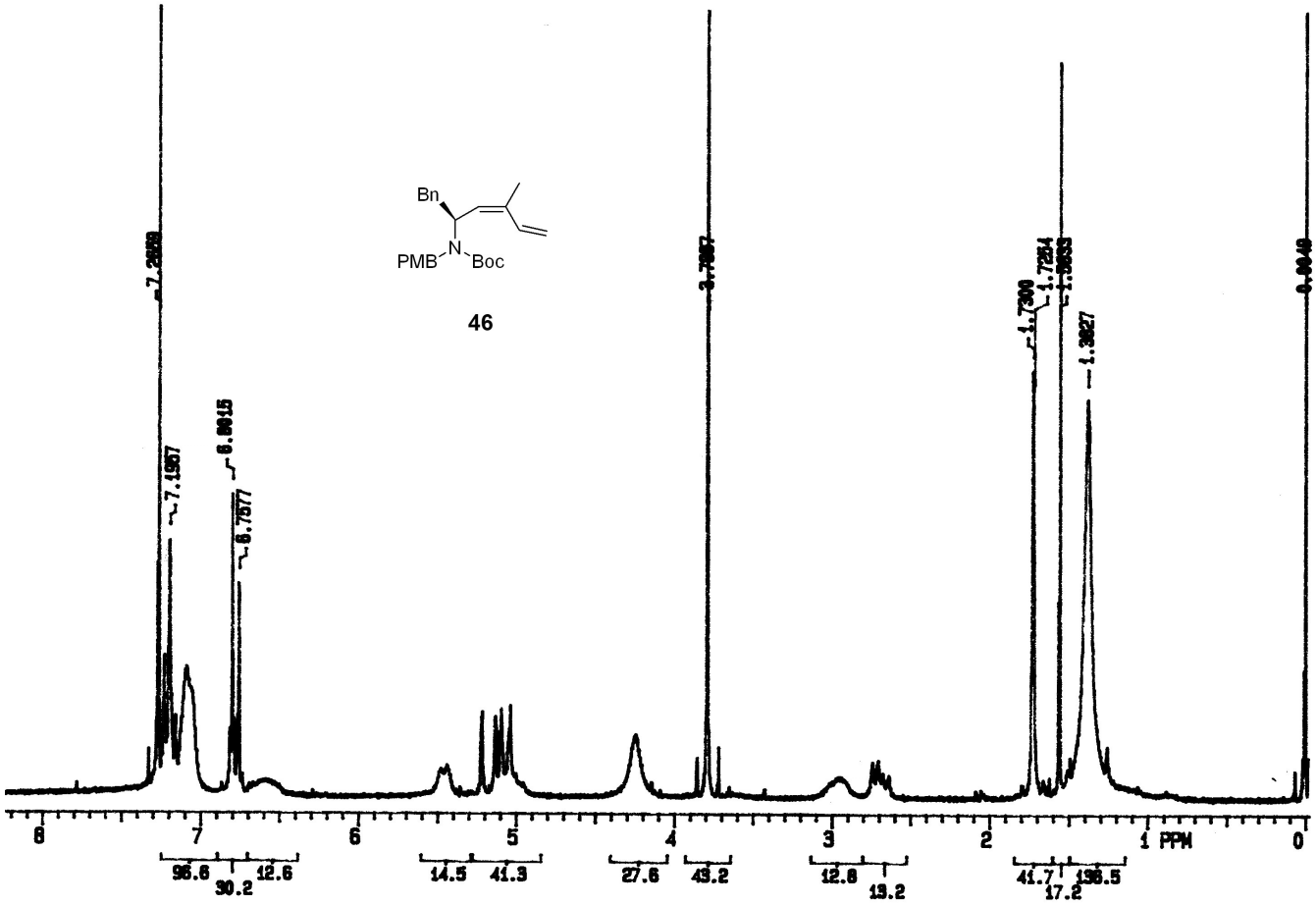

Bn
OH
PMB
N
Boc
7.2669
7.2570
7.2211
7.2069
7.1753
7.1304
6.8605
6.8163
4.3279
3.8039
1.8696
1.8604
0.0084
100.1
26.3
13.1
10.7
25.8
50.9
13.2
12.0
11.8
46.8
119.7
1 PPM

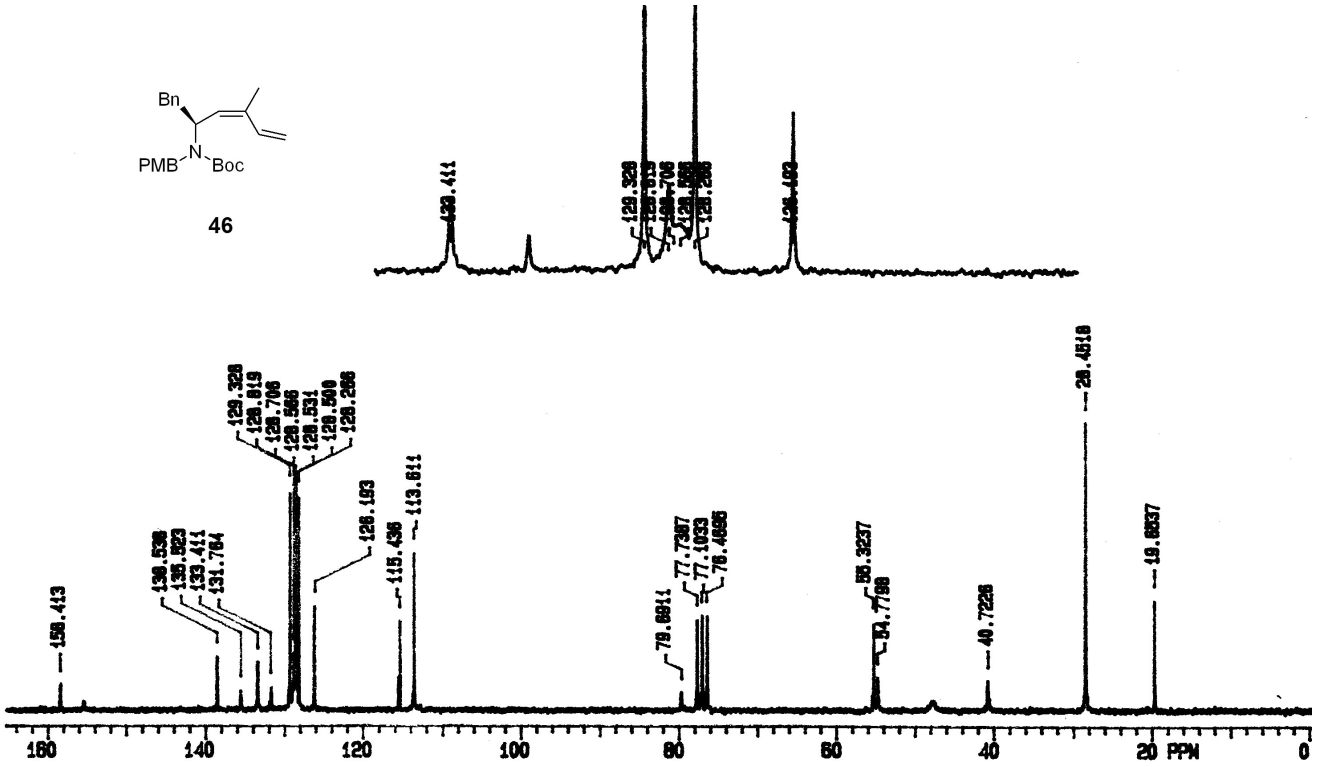
44

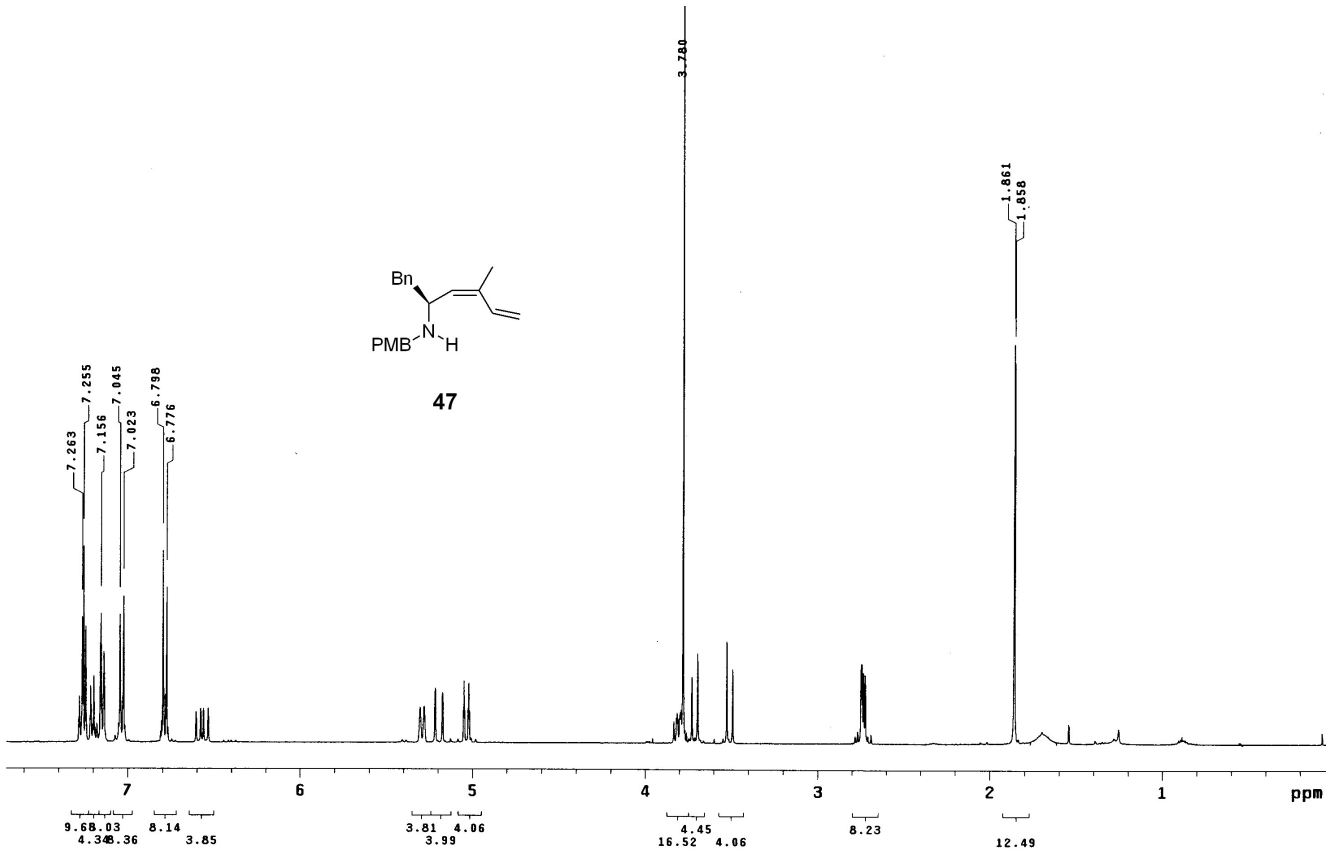

Bn
OH
PMB
N
Boc
44
159.576
155.835
138.496
131.755
129.369
128.470
128.342
126.431
125.601
113.711
113.824
80.2650
77.7817
77.1182
76.4784
61.4579
55.3464
47.4889
40.8863
40.5196
28.4984
21.7940
160
140
120
100
80
60
40
20 PPM
0

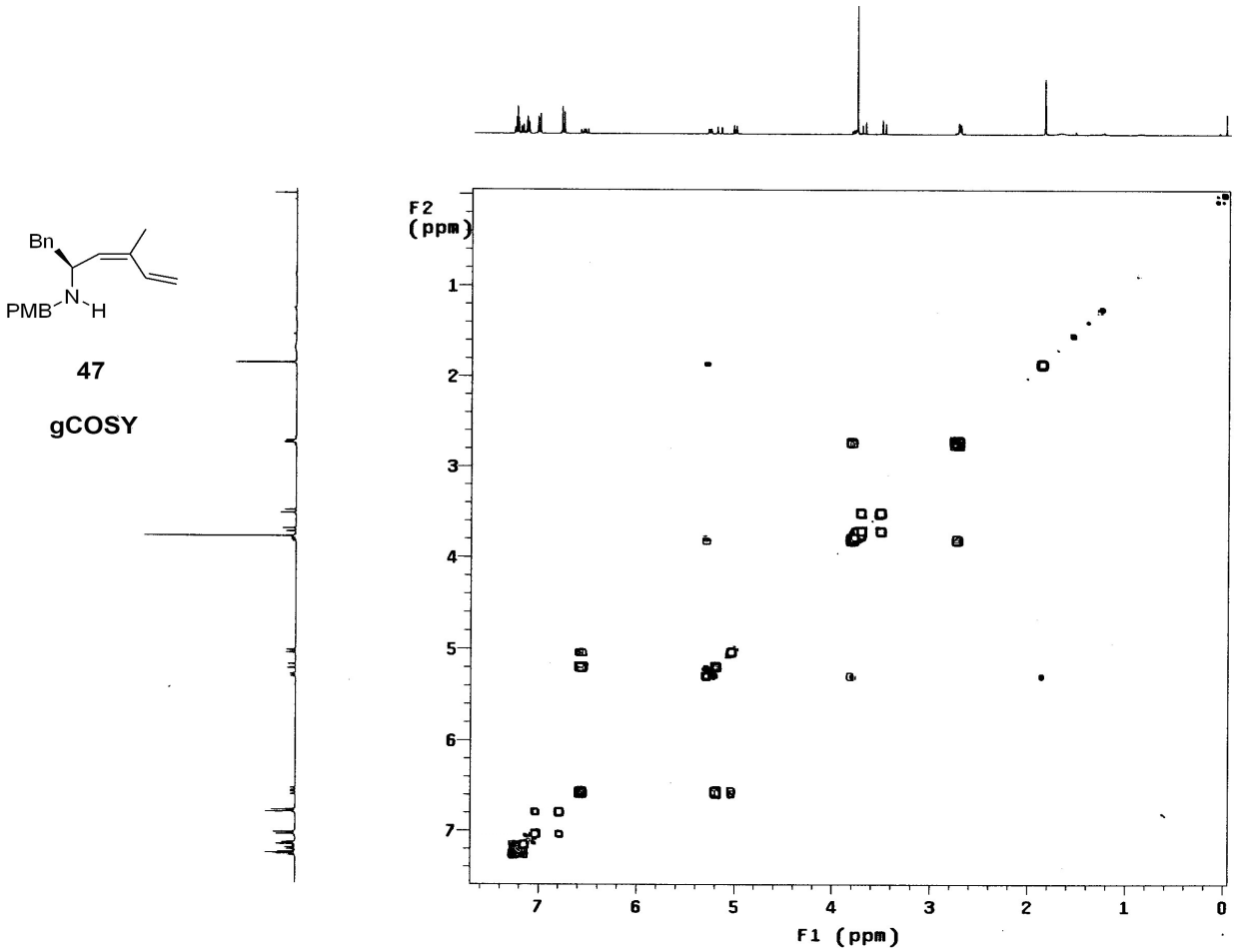

Bn
O
PMB
N
Boc
45
9.6666
7.2676
7.2661
7.2484
7.2119
7.0638
6.8401
6.7984
3.7579
1.6376
1.4810
0.0069
0.0038
10
9
8
7
6
5
4
3
2
1 PPM
0
17.5
67.7
69.7
32.9
15.0
18.3
34.2
51.9
17.8
18.9
63.5
150.6

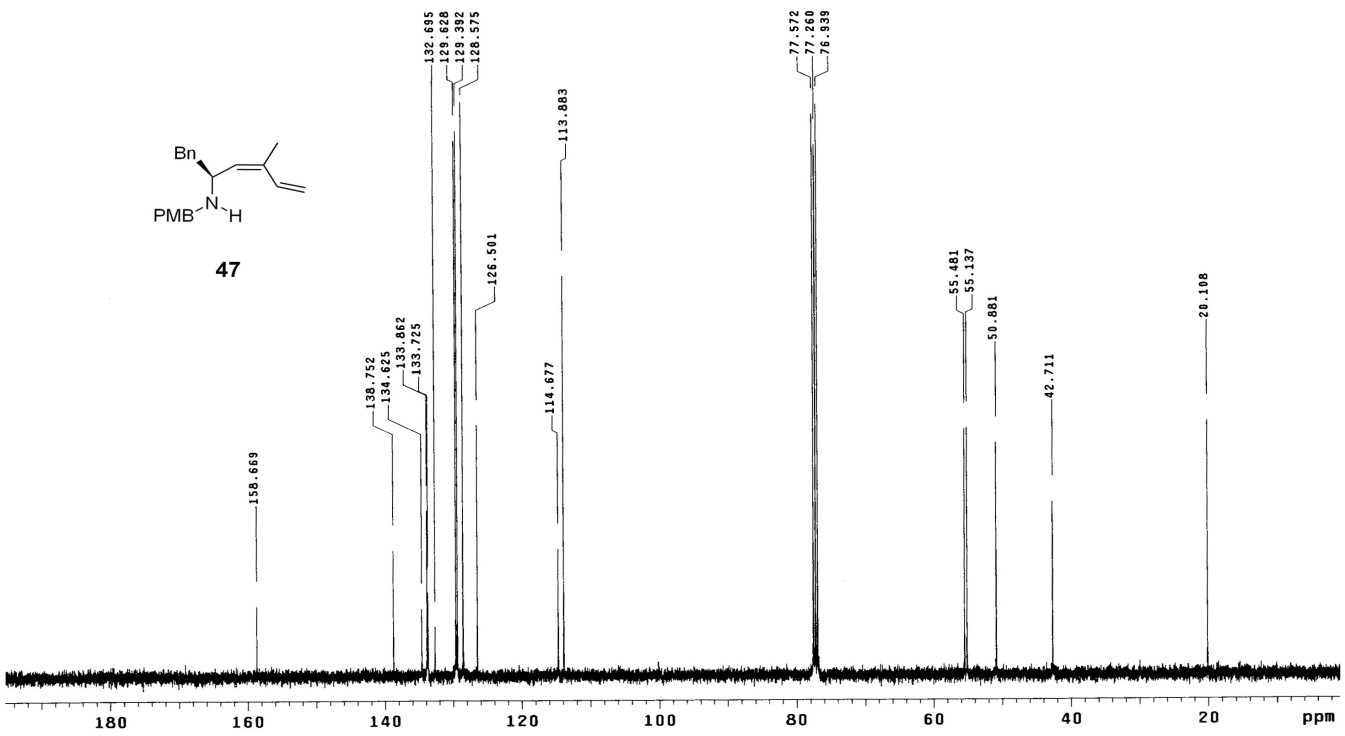

Bn
PMB
N
Boc
O
45
200
180
160
140
120
100
80
60
40
20 PPM

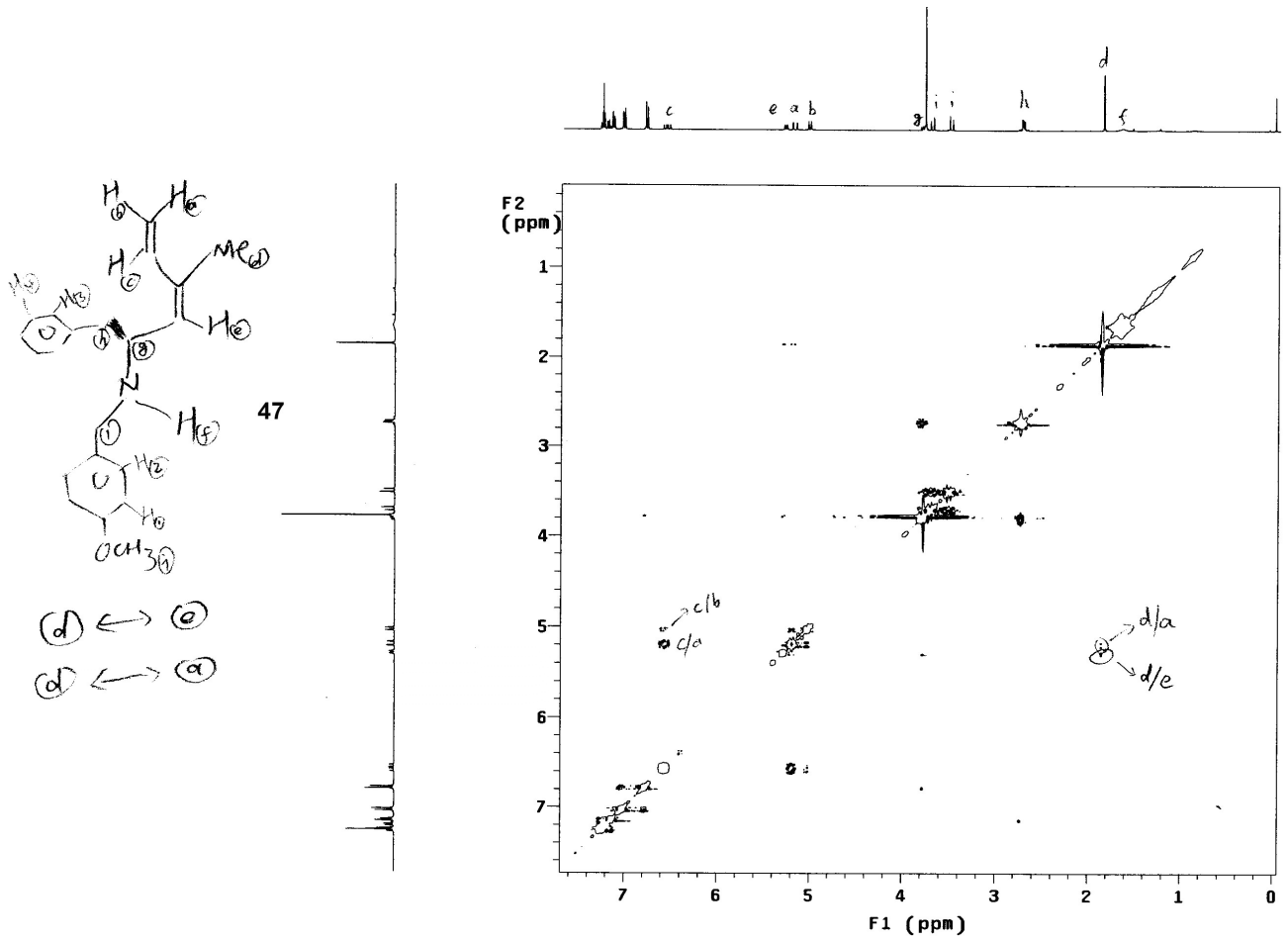

Bn
PMB
N
Boc
46
7.1957
6.7677
1.7300
1.3827
6
7
5
4
3
2
1 PPM
0
96.6
90.2
12.6
14.5
41.3
27.6
43.2
12.8
19.2
41.7
17.2
136.5

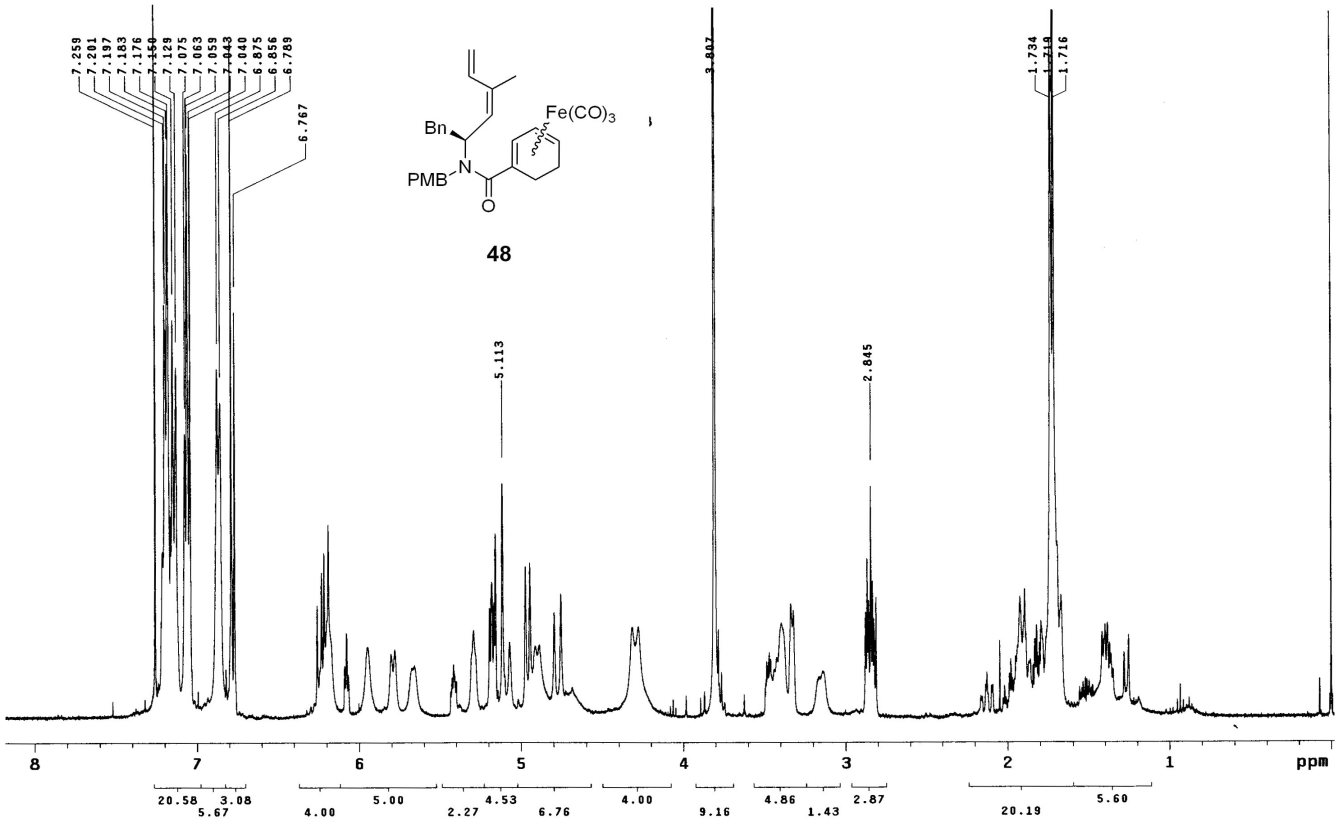

Bn
PMB
N
Boc
46
159.413
130.538
130.023
133.411
131.764
129.328
129.019
128.706
128.566
128.531
128.500
128.266
126.193
115.436
113.611
79.6911
77.7387
77.1033
76.4686
55.3237
54.7798
40.7226
28.4518
19.8537
160
140
120
100
80
60
40
20 PPM
0


Bn
PMB
N
H
47
3.780
1.861
1.858
7.263
7.255
7.156
7.045
7.023
6.798
6.776
7
6
5
4
3
2
1
ppm
9.68
8.03
4.34
8.36
8.14
3.85
3.81
4.06
3.99
4.45
16.52
4.06
8.23
12.49


Bn
PMB
N
H
47
gCOSY
F2
(ppm)
F1 (ppm)


Bn
PMB
N
H
47
132.695
129.628
129.382
128.575
113.883
77.572
77.260
76.939
126.501
55.481
55.137
50.881
42.711
20.108
138.752
134.625
133.862
133.725
114.677
158.669
ppm


47
F2 (ppm)
F1 (ppm)
(d) ⟷ (e)
(d) ⟷ (a)
c/b
c/a
d/a
d/e


48
Bn
PMB
N
O
Fe(CO)3
7.259
7.201
7.197
7.183
7.176
7.150
7.129
7.075
7.063
7.059
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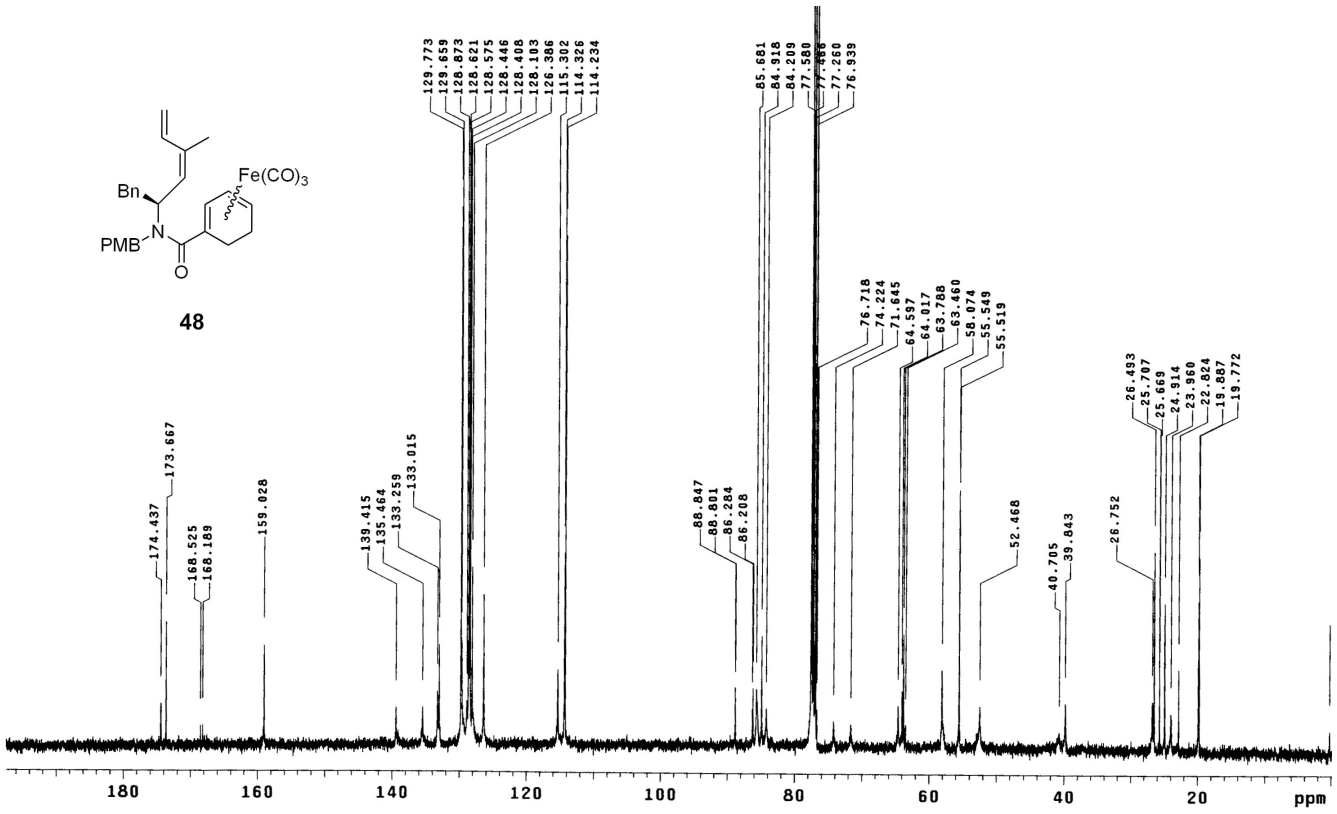
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80
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20
ppm