Supporting Information

Readily Available Hydrogen-Bond Catalysts for the Asymmetric Transfer Hydrogenation of Nitroolefins

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1. General Information

^{1}H NMR spectra were recorded on a 250 MHz and 400 MHz spectrometer. Chemical shifts are reported in ppm with $CHCl_3$, acetone or DMSO as an internal standard ($CHCl_3$: 7.26 ppm; acetone: 2.05 ppm; DMSO: 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, b = broad, m = multiplet), integration and coupling constants (Hz). ^{13}C NMR spectra were recorded on a 63 MHz and 101 MHz NMR spectrometer. Chemical shifts are reported in ppm with $CHCl_3$, acetone or DMSO as an internal standard ($CHCl_3$: 77.2 ppm; acetone: 29.8 ppm; DMSO: 39.5 ppm). MS: The molecular fragments are quoted as the relation between mass and charge (*m/z*), the intensities as a percentaged value relative to the intensity of the base signal (100%). The abbreviation $[M]^+$ refers to the Molecule-Ion. IR spectra were collected as KBr pellets or as solids (platinum ATR and DRIFT). The deposit of the absorption band was given in wave numbers $\tilde{\nu}$ in cm^{-1}. Unless otherwise specified, all starting materials, reagents and solvents are commercially available and were used without further purification. Flash column chromatography was carried out on silica gel. Routine monitoring of reactions were performed using silica gel coated aluminum plates (silica gel 60, F_{254}). All reactions involving moisture sensitive reactants were executed under an argon atmosphere using oven dried glassware.

2. Experimental and Characterization Data

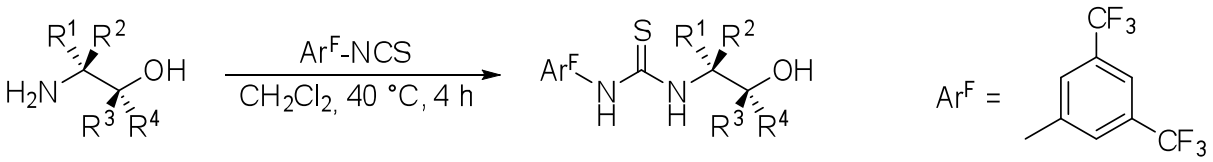
x2.1. Preparation of the catalysts

General Procedure for the preparation of the catalysts **1a-p** and **7**

General procedures for the synthesis of aminoalcohol-derived thioureas

Catalysts **1a-1c** and **1g-1p** were synthesized following procedure A, catalysts **1d-1f** according to procedure B, and catalyst **7** as described below individually.

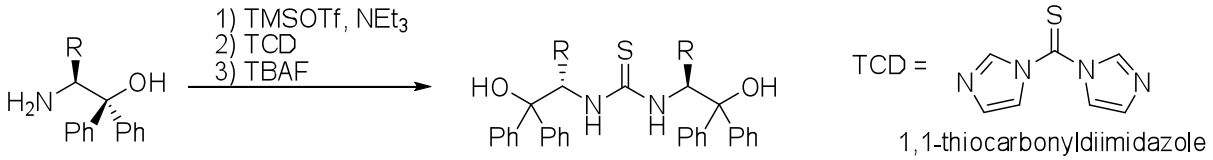
Procedure A



To a solution of the respective aminoalcohol (6.61 mmol, 1.00 equiv.) in dry CH_2Cl_2 (7.0 mL) was added 3,5-bis(trifluoromethyl)phenylisothiocyanate (1.33 mL, 7.27 mmol, 1.10 equiv.). After stirring at 40 °C for 3 h, the solvent was removed under reduced pressure. The residue was subjected to flash chromatography (SiO_2, cyclohexane/ethyl acetate) to give the title compound as an off-white solid.

The aminoalcohols, if not commercially available, were synthesized through Grignard reaction of the respective amino acid esters with phenylmagnesiumbromide, following a standard procedure published by *Zhou et al*.[1]

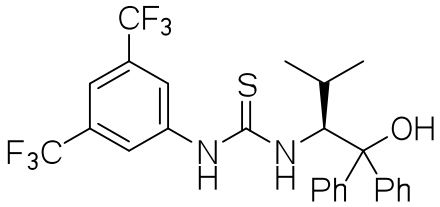
Procedure B



[1] Kang, Y. F.; Liu, L.; Wang, R.; Yan, W. J.; Zhou, Y. F. *Tetrahedron Asymmetry* **2004**, *15*, 3155.

To a solution of the aminoalcohol (4.12 mmol) in dry $CHCl_3$ (10 mL) was added NEt_3 (5.36 mmol). The reaction was cooled to 0 °C, and trimethylsilyltriflate (5.36 mmol) was added. The reaction was stirred for 16 h at r.t. and sat. $NaHCO_3$ was added. The layers were separated and the aqueous layer was washed with $CHCl_3$ (3 × 25 mL). The combined organic layer was dried over $MgSO_4$, filtered and the volatiles were removed. The crude product was used without further purification (The product can be purified with column chromatography (cyclohexane/ethyl acetate 80/20 v/v)). A solution of the hydroxy-protected aminoalcohol (5.00 mmol) in dry THF (2 mL) was added to a solution of 1,1-thiocarbonyldiimidazole (3.00 mmol) in dry THF (3 mL). The reaction was stirred at r.t. for 72 h. Deprotection of the silylated compound was conducted subsequently. The mixture was cooled to 0 °C and tetrabutylammonium fluoride (5.5 mmol, 1M) was added. The mixture was stirred for 16 h at r.t.. The reaction was diluted with THF (5 mL) and H_2O (5 mL) was added. The layers were separated and the aqueous layer was washed with Et_2O (3×). The combined organic layer was dried over $MgSO_4$, filtered and the volatiles were removed. The residue was subjected to column chromatography (cyclohexane/ethyl acetate 80/20 or 90/10 v/v)) to yield the title compound as white solids.

Synthesis of *N*-((*S*)-(2-amino-3-methyl-1,1-diphenyl-butan-1-ol))-*N'*-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**1a**)

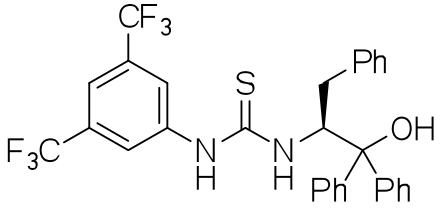


Compound **1a** was obtained according to general procedure A, using (S)-1,1-diphenylvalinol (500 mg, 1.96 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 90/10 v/v). The compound was obtained as a white foamy solid (1.05 g, 2.80 mmol, 85%). m.p. 70 °C (capillary); (lit.[2]: 66-68 °C); R_f (cyclohexane/ethyl acetate, 90:10) = 0.49; $[\alpha]^{20}_D$ = –28.0 (c = 0.5, $CHCl_3$); (lit.[2]: –16.7 (c = 0.32, $CHCl_3$);

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.60 (br s, 1H, NH), 7.70–7.15 (m, 13H, H_{Ar}), 6.93–6.86 (m, 1H, CH), 5.58 (br s, 1H, NH), 2.81 (br s, 1H, OH), 2.01–1.98 (m, 1H, $CH(CH_3)_2$), 1.03 (d, *J* = 6.8 Hz, 3H, CH_3), 0.85 (d, *J* = 6.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.5 (C=S), 144.9 (C_{Ar}), 144.3 (C_{Ar}), 138.4 (C_{Ar}), 133.0 (2C, $^2J_{CF}$ = 33.8 Hz, C_{Ar}–CF_3), 128.6 (4C, CH_{Ar}), 127.4 (CH_{Ar}), 127.3 (CH_{Ar}), 125.3 (2C, CH_{Ar}), 125.1 (2C CH_{Ar}), 123.9 (2C, CH_{Ar}), 122.7 (2C, $^1J_{CF}$ = 273.1 Hz, CF_3), 119.4 (CH_{Ar}), 83.2 (C-OH), 63.6 (CH), 29.7 (CH_3), 23.4 (CH_3), 18.4 ($CH(CH_3)_2$); ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.86 (m, 6F, CF_3); IR (KBr): ṽ = 3445 (w), 3278 (m), 3218 (w), 3064 (w), 2959 (w), 2875 (vw), 1951 (vw), 1801 (vw), 1623 (vw), 1542 (m), 1468 (m), 1385 (m), 1277 (s), 1150 (s), 1046 (w), 967.2 (w), 895.5 (m), 847.9 (w), 743.4 (w), 702.2 (m), 682.7 (m), 636.9 (w), 540.3 (w); EI-MS *m/z* (%): 526.3 (5) $[M]^+$, 492.4 (39), 466.2 (15) $[M - C_3H_7OH)^+$, 344.2 (40) $(C_{13}H_{14}F_6N_2S]^+$, 43.0 (100); HR-EIMS calcd for $C_{26}H_{24}F_6N_2OS$: 526.1514, found: 526.1511. Analytical data is in agreement with the literature.[2]

[2] Lattanzi, A. *Synlett* **2007**, *13*, 2106.

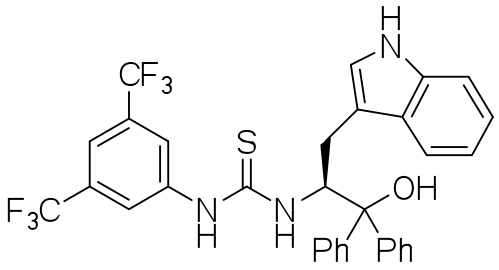
Synthesis of *N*-((*S*)-(2-amino-1,1,3-triphenyl-propane-1-ol))-*N*'-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**1b**)



Compound **1b** was obtained according to general procedure A, using (*S*)-1,1-diphenylphenylalaninol (1.00 g, 3.30 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 90/10 v/v). The compound was obtained as a white foamy solid (1.42 g, 2.47 mmol, 75%). m.p. 85 °C (capillary); (lit.[2]: 79-82 °C); R_f (cyclohexane/ethyl acetate, 90:10) = 0.47; $[\alpha]^{20}_D$ = –98.1 (c = 0.5, $CHCl_3$); (lit.[2]: –75.1 (c = 0.33, $CHCl_3$);

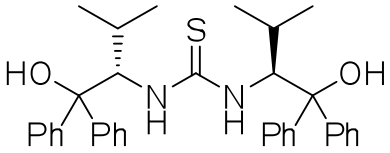
^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.17 (br s, 1H, NH), 7.59–6.76 (m, 20H, 18 × H_{Ar}, 1 × NH, 1 × CH), 5.85 (br s, 1H, OH), 3.20–2.90 (m, 1H, CH_2), 2.77 (dd, ^2J = 7.0 Hz, ^3J = 14.1 Hz, 1H, CH_2); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 179.8 (C=S), 144.2 (C_{Ar}), 143.7 (C_{Ar}), 138.4 (C_{Ar}), 138.1 (C_{Ar}), 132.6 (2C, J_{CF} = 33.8 Hz, C_{Ar}–CF_3), 129.5 (2C, CH_{Ar}), 128.7 (2C, CH_{Ar}), 128.6 (2C, CH_{Ar}), 127.5 (2C, CH_{Ar}), 127.4 (2C, CH_{Ar}), 126.9 (CH_{Ar}), 125.3 (2C, CH_{Ar}), 125.1 (2C, CH_{Ar}), 122.9 (2C, J_{CF} = 273.8 Hz, CF_3), 124.0 (2C, CH_{Ar}), 119.6–119.1 (m, CH_{Ar}), 81.9 (C-OH), 60.8 (CH), 35.7 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.87 (m, 6F, CF_3); FTIR (KBr): $\tilde{\nu}$ = 3322 (w), 3063 (w), 1962 (vw), 1897 (vw), 1806 (vw), 1603 (w), 1534 (w), 1473 (w), 1450 (w), 1381 (w), 1278 (m), 1181 (w), 1136 (w), 1057 (vw), 1033 (w), 972 (w), 888 (w), 848 (vw), 767 (w), 750 (w), 701 (w), 681 (w); EI-MS m/z (%): 575.2 (30) $[M + H]^+$, 574.2 (88) $[M]^+$, 556.2 (54), 555.2 (56), 540.2 (100), 537.2 (30). HR-EIMS calcd for $C_{30}H_{24}F_6N_2OS$: 574.1517, found: 574.1514 $[M]^+$. Analytical data is in agreement with the literature.[2]

Synthesis of *N*-((*S*)-(2-amino-3-(indole-3-yl)-1,1-diphenyl-propane-1-ol))-*N'*-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**1c**)



Compound **1c** was obtained according to general procedure A, using (*S*)-1,1-diphenyltryptophanol (500 mg, 1.46 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 80/20 v/v). The compound was obtained as a white foamy solid (712 mg, 1.16 mmol, 80%). m.p. 183 °C (capillary); R_f (cyclohexane/ethyl acetate, 70:30) = 0.61 ; $[\alpha]^{20}_D$ = –43.4 (c = 0.5, $CHCl_3$; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.90 (br s, 1H, NH), 8.09–8.03 (m, 1H, H_{Ar}), 7.93–7.88 (m, 2H, H_{Ar}), 7.71–7.60 (m, 5H, H_{Ar}), 7.45–7.04 (m, 10H, 8 × H_{Ar}, 2 × NH), 7.00–6.93 (m, 1H, H_{Ar}), 6.91–6.83 (m, 1H, H_{Ar}), 6.26 (br s, 1H, OH), 5.88 (dt, *J* = 9.8 Hz, *J* = 2.6 Hz, 1H, CH), 3.20–2.90 (m, 1H, CH_2), 2.85 (dd, *J* = 14.6 Hz, *J* = 2.0 Hz, 1H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.4 (C=S), 146.0 (C_{Ar}), 145.8 (C_{Ar}), 141.8 (C_{Ar}), 135.9 (CH_{Ar}), 129.8 (2C, J_{CF} = 33.8 Hz, C_{Ar}–CF_3), 128.1 (2C, CH_{Ar}), 127.8 (CH_{Ar}), 127.2 (2C, CH_{Ar}), 126.5 (CH_{Ar}), 126.1 (2C, CH_{Ar}), 125.6 (C_{Ar}), 125.5 (2C, CH_{Ar}), 125.3 (C_{Ar}), 124.4 (C_{Ar}), 121.9 (2C, J_{CF} = 272.7 Hz, CF_3), 121.5 (2C, CH_{Ar}), 117.9 (CH_{Ar}), 117.7 (CH_{Ar}), 115.7 (CH_{Ar}), 110.9 (CH_{Ar}), 110.6 (CH_{Ar}), 80.7 (C-OH), 59.8 (CH), 26.2 (CH_2); ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.87 (m, 6F, CF_3); FTIR (KBr): $\tilde{\nu}$ = 3394 (m), 3302 (m), 3090 (w), 3054 (w), 2932 (vw), 1620 (w), 1551 (m), 1498 (m), 1446 (w), 1419 (w), 1373 (m), 1341 (m), 1280 (s), 1250 (m), 1178 (m), 1130 (s), 1110 (m), 1095 (m), 1059 (w), 980.2 (w), 887.1 (m), 747.6 (m), 734.0 (w), 698.9 (m), 681.8 (m), 661.2 (w), 547.7 (w), 428.4 (w); EI-MS m/z (%): 613.2 (100) $[M]^+$, 450.1 (65), 430.1 (60) $[M - C_{13}H_{11}O]^+$, 397.1 (15), 271.0 (48), 213.1 (10) $[C_8H_3F_6]^+$, 130.1 (32), $[C_9H_8N]^+$, 43 (41); HR-EIMS calcd for $C_{32}H_{25}F_6N_3OS$: 613.1623, found: 613.1621; elemental analysis calcd (%) for $C_{32}H_{25}F_6N_3OS$: N 6.85, C 62.64, H 4.11, S 5.23, found: N 6.78, C 62.28, H 4.04, S 5.20.

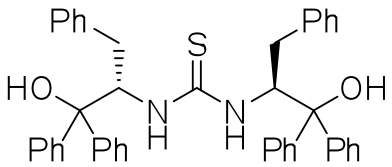
Synthesis of 1,3-bis((*S*)-1-hydroxy-3-methyl-1,1-diphenylbutan-2-yl)thiourea (**1d**)



Compound **1d** was obtained according to general procedure B, using (*S*)-1,1-diphenylvalinol (1.05 g, 4.12 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 95/5 v/v). The compound was obtained as a white foamy solid (1.08 g, 1.96 mmol, 48%). m.p. 191 °C (capillary); R_f (cyclohexane/ethyl acetate, 90:10) = 0.50 ; $[\alpha]^{20}_D$ = –98.1 (c = 0.5, $CHCl_3$);

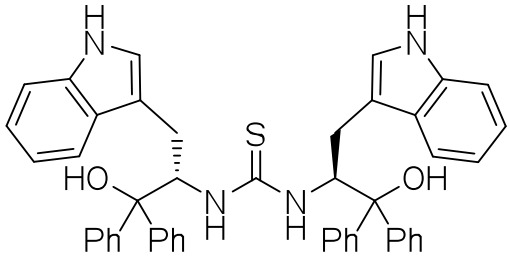
^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.13 (s, 2H, NH), 7.55–7.47 (m, 4H, H_{Ar}), 7.41–7.27 (m, 16H, H_{Ar}), 4.49 (d, *J* = 4.0 Hz, 2H, CH), 1.95 – 1.79 (m, 2H, CH), 1.71 (br s, 2H, OH), 0.91 (d, *J* = 6.1 Hz, 6H, CH_3), 0.69 (d, *J* = 6.4 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.9 (C_q, C=S), 142.3 ($2C_q$, C_{Ar}), 138.1 ($2C_q$, C_{Ar}), 128.7 (6C, CH_{Ar}), 128.2 (6C, CH_{Ar}), 126.9 (4C, CH_{Ar}), 125.7 (4C, CH_{Ar}), 95.7 (2C, C-OH), 69.5 (2C, CH), 29.7 (2C, CH), 20.9 (2C, CH_3), 16.3 (2C, CH_3); FTIR (KBr): $\tilde{\nu}$ = 3275 (w), 3061 (w), 2964 (w), 2933 (w), 2874 (w), 1501 (m), 1448 (w), 1345 (w), 1266 (m), 1170 (m), 1122 (w), 1105 (w), 971 (w), 904 (w), 834 (w), 702 (m), 635 (w), 606 (w); EI-MS m/z (%): 553.3 (26) $[M]^+$, 535.3 (22) $[M – OH]^+$, 369.2 (25) $[M – C_{13}H_{11}O]^+$, 298.1 (100) $[M – C_{17}H_{20}NO]^+$, 238.1 (100) $[M – C_{17}H_{19}O]^+$; HR-EIMS calcd for $C_{35}H_{41}N_2O_2S$: 553.2889, found: 553.2891 $[M]^+$.

Synthesis of 1,3-bis((*S*)-1-hydroxy-1,1,3-triphenylpropan-2-yl)thiourea (**1e**)



Compound **1e** was obtained according to general procedure B, using (*S*)-1,1-diphenylphenylalanin (1.35 g, 4.45 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 80/20 v/v). The compound was obtained as a white foamy solid (1.23 g, 1.91 mmol, 43%). m.p. 93 °C (capillary); R_f (cyclohexane/ethyl acetate, 80:20) = 0.26 ; $[\alpha]^{20}_D$ = –82.6 (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO): δ = 10.3 (br s, 2H, NH), 7.65–7.63 (m, 4H, H_{Ar}), 7.44–7.28 (m, 16H, H_{Ar}), 7.27–7.16 (m, 6H, H_{Ar}), 7.13–7.09 (m, 4H, H_{Ar}), 5.05 (dd, *J* = 9.5, Hz, *J* = 4.6 Hz, 2H, CH), 3.34 (br s, 2H, OH), 2.59 (dd, *J* = 13.9 Hz, *J* = 4.6 Hz, 2H, CH_2), 2.33-2.27 (m, 2H, CH_2); ^{13}C NMR (100 MHz, DMSO): δ = 185.9 (C=S), 142.4 (2C, C_{Ar}), 138.4 (2C, C_{Ar}), 136.2 (2C, C_{Ar}), 129.2 (4C, CH_{Ar}), 128.4 (4C, CH_{Ar}), 128.3 (2C, CH_{Ar}), 128.2 (4C, CH_{Ar}), 128.1 (4C, CH_{Ar}), 127.8 (2C, CH_{Ar}), 126.3 (2C, CH_{Ar}), 125.9 (4C, CH_{Ar}), 125.5 (4C, CH_{Ar}), 94.0 (2C, C-OH), 63.6 (2C, CH), 38.0 (2C, CH_2); FTIR (KBr): $\tilde{\nu}$ = 3418 (vw), 3188 (vw), 3061 (vw), 3028 (vw), 2955 (vw), 1601 (vw), 1449 (vw), 1343 (vw), 1267 (vw), 1170 (vw), 1066 (vw), 1031 (vw), 967 (vw), 931 (vw), 755 (vw), 698 (w), 529 (vw); FAB-MS m/z (%): 649.2 (15) $[M]^+$, 631.2 $[M – OH]^+$, 465.1 (25) $[C_{30}H_{29}N_2OS]^+$, 447.1 (20) $[C_{30}H_{28}N_2S]^+$, 346.1 (60) $[C_{22}H_{20}NOS]^+$, 91.1 (100); HR-FABMS calcd for $[C_{43}H_{41}N_2O_2S]^+$: 649.2888, found: 649.2891 $[M + H]^+$.

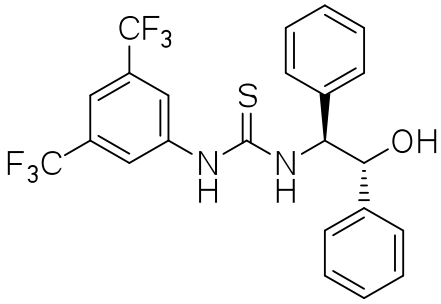
Synthesis of 1,3-bis((*S*)-1-hydroxy-3-(indol-3-yl)-1,1-diphenylpropan-2-yl)thiourea (**1f**)



Compound **1f** was obtained according to general procedure B, using (*S*)-1,1-diphenyltryptophanol (1.00 g, 2.93 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 75/25 v/v). The compound was obtained as a white foamy solid (0.81 g, 1.11 mmol, 38%). m.p. 163 °C (capillary); R_f (cyclohexane/ethyl acetate, 75:25) = 0.22 ; $[\alpha]^{20}_D$ = –244.6 (c = 0.5, $CHCl_3$);

^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.20 (s, 2H, NH), 7.55–7.47 (m, 6H, H_{Ar}), 7.42–7.31 (m, 18H, 14 × H_{Ar}, 2 × NH, 2 × OH), 7.23–7.11 (m, 8H, H_{Ar}), 6.87 (d, *J* = 2.1 Hz, 2H, H_{Ar}), 4.92 (dd, *J* = 11.2 Hz, *J* = 3.1 Hz, 2H, CH), 2.76 (dd, *J* = 14.5, *J* = 2.6 Hz, 2H, CH_2), 2.36 (dd, *J* = 14.5 Hz, *J* = 11.7 Hz, 2H, CH_2); ^{13}C NMR (63 MHz, $CDCl_3$): δ = 187.8 (C=S), 141.1 (2C, C_{Ar}), 138.2 (2C, C_{Ar}), 136.5 (2C, C_{Ar}), 128.8 (2C, CH_{Ar}), 128.7 (6C, CH_{Ar}), 128.5 (6C, CH_{Ar}), 126.6 (4C, CH_{Ar}), 126.1 (4C, CH_{Ar}), 122.8 (2C, C_{Ar}), 120.1 (2C, CH_{Ar}), 118.1 (2C, CH_{Ar}), 111.6 (2C, CH_{Ar}), 110.2 (2C, C_{Ar}), 95.5 (2C, CH_{Ar}), 63.9 (2C, C-OH), 28.9 (2C, CH), 26.9 (2C, CH_2). FTIR (KBr): $\tilde{\nu}$ = 3413 (w), 3058 (w), 2924 (w), 2848 (w), 1724 (vw), 1618 (vw), 1494 (m), 1448 (w), 1339 (w), 1267 (w), 1170 (m), 1094 (w), 1010 (vw), 965 (w), 930 (w), 902 (vw), 789 (vw), 743 (w), 699 (m), 631 (vw), 578 (w), 539 (w), 429 (vw) cm^{-1}; EI-MS m/z (%) 727.2 (60) $[M]^+$, 649.1 (4) $[M - C_6H_5]^+$, 543.1 (73) $[M - C_{13}H_{11}O]^+$, 384.1 (100) $[M - C_{24}H_{21}N_2OS]^+$, 309.1 (56) $[M - C_{23}H_{19}N]^+$; HR-EIMS calcd for $C_{47}H_{42}N_4O_2S$: 726.3028, found: 726.3029 $[M]^+$.

Synthesis of *N*-((1*R*,2*S*)-(2-amino-1,2-diphenylethanol))-*N*'-(3,5-bis-(trifluoro-methyl)-phenyl)-thiourea (**1g**)

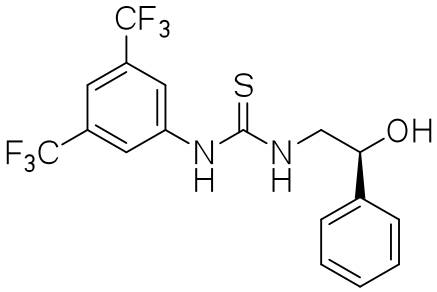


Compound **1g** was obtained according to general procedure A, using (1*R*,2*S*)-2-amino-1,2-diphenylethanol (500 mg, 2.34 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 80/20 v/v). The compound was obtained as a white foamy solid (1.06 g, 2.19 mmol, 94%). m.p. 65 °C (capillary) (lit.[3]: 62 °C); R_f (cyclohexane/ethyl acetate, 80:20) = 0.23; $[\alpha]^{20}_D$ = 54.5 (c = 0.5, $CHCl_3$), (lit.[3]: +112.0 (c = 1.12, $CHCl_3$);

^{1}H NMR (250 MHz, $CDCl_3$): δ = 10.36 (br s, 1H, NH), 8.73 (br d, *J* = 8.8 Hz, 1H, NH), 8.29 (s, 2H, H_{Ar}), 7.73 (s, 1H, H_{Ar}), 7.34–7.01 (m, 10H, H_{Ar}), 5.87 (br. d, J = 4.3 Hz, 1H, OH), 5.71–5.61 (m, 1H, CH), 5.18–5.09 (m, 1H, CH) ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 179.5 (C=S), 142.1 (C_{Ar}), 141.8 (C_{Ar}), 137.9 (C_{Ar}), 130.1 (q, *J* =31.1 Hz, 2C, CCF_3), 128.6 (2C, CH_{Ar}), 127.5 (2C, CH_{Ar}), 127.2 (2C, CH_{Ar}), 126.9 (CH_{Ar}), 126.8 (CH_{Ar}), 126.3 (2C, CH_{Ar}), 123.1 (q, *J* =272.8 Hz, 2C, CF_3), 121.5 (2C, CH_{Ar}), 116.2–115.8 (m, CH_{Ar}), 74.0 (CH), 62.8 (CH) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.9 (m, 6F, CF_3) ppm; FTIR (Platinum ATR): $\tilde{\nu}$ = 3279 (w), 3065 (w), 2929 (vw), 1953 (vw), 1806 (vw), 1528 (m), 1472 (w), 1382 (m), 1279 (m), 1170 (m), 1137 (m), 1055 (w), 1001 (vw), 958 (w), 888 (w), 848 (vw), 749 (vw), 701 (m), 682 (m), 587 (vw) cm^{-1}; MS (FAB), m/z (%): 485.1 (100) $[M + H]^+$, 467.1 (20) $[M – OH]^+$, 378.1 (15) $[C_{16}H_{12}F_6N_2S]^+$, 289.1 (20) $[C_9H_7F_6N_2S]^+$, 196.3 (80) $[C_{14}H_{12}O]^+$ 105.4 (20); HR-FABMS calcd for $C_{23}H_{19}F_6N_2OS$: 485.1122, found 485.1125 $[M + H]^+$. Analytical data is in accordance with the literature.[3]

[3] Sibi, M.; Itoh, K. *J. Am. Chem. Soc.* **2007**, *129*, 8064.

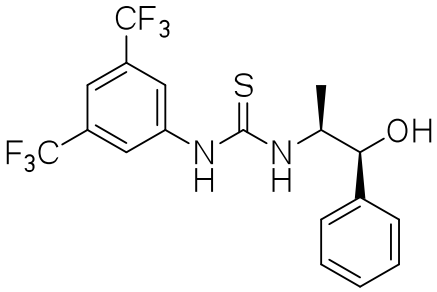
Synthesis of *N*-((*S*)-(2-amino-1-phenylethanol))-*N*'-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**1h**)



Compound **1h** was obtained according to general procedure A, using (*S*)-2-amino-1-phenylethanol (600 mg, 4.97 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 80/20 to 60/40 v/v). The compound was obtained as a white foamy solid (1.85 g, 4.52 mmol, 91%). m.p. 147.3 °C (capillary) (lit.[2]: 145-147 °C); R_f (cyclohexane/ethyl acetate, 80:20) = 0.20; $[\alpha]^{20}_D$ = –74.2 (c = 0.5, $CHCl_3$), (lit.[2]: –55.0 (c = 0.30, $CHCl_3$);

^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.57 (br s, 1H, NH), 8.36 (s, 2H, H_{Ar}), 7.80 (br s, 1H, NH), 7.72 (s, 1H, H_{Ar}), 7.52–7.44 (m, 2H, H_{Ar}), 7.42–7.23 (m, 3H, H_{Ar}), 5.12–5.01 (m, 1H, CH), 4.82 (br s, 1H, OH), 4.19–3.97 (m, 1H, CH_2), 3.69–3.51 (m, 1H, CH_2) ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 183.5 (C=S), 144.9 (C_{Ar}), 143.9 (C_{Ar}), 132.9 (q, *J* =32.3 Hz, 2C, CCF_3), 130.1 (2C, CH_{Ar}), 129.3 (CH_{Ar}), 127.7 (2C, CH_{Ar}), 125.5 (q, *J* =271.0 Hz, 2C, CF_3), 124.3 (2C, CH_{Ar}), 118.6–118.3 (m, CH_{Ar}), 73.2 (CH), 53.8 (CH_2) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.9 (m, 6F, CF_3) ppm; FTIR (Platinum ATR): $\tilde{\nu}$= 3382 (vw), 3234 (vw), 3067 (vw), 1818 (vw), 1555 (w), 1493 (vw), 1467 (vw), 1369 (w), 1272 (m), 1172 (m), 1153 (w), 1126 (m), 1062 (w), 1028 (vw), 948 (m), 925 (vw), 904 (vw), 890 (m), 847 (vw), 767 (vw), 743 (vw), 700 (m), 679 (m), 619 (vw), 584 (vw), 530 (vw), 421 (vw) cm^{-1}; MS (FAB), m/z (%): 409.0 (100) $[M + H]^+$, 391.0 (20) $[M - OH]^+$, 289.6 (55) $[C_9H_7F_6N_2S]^+$, 121.9 (40) $[C_8H_9O]^+$; HR-FABMS calcd for $C_{17}H_{15}F_6N_2OS$: 409.0809, found 409.0811 $[M + H]^+$. Analytical data is in accordance with the literature.[2]

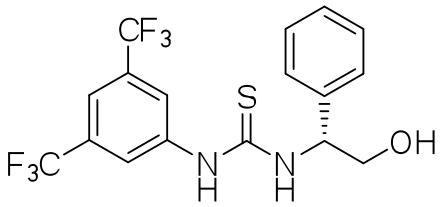
Synthesis of *N*-((1*R*,2*S*)-(2-amino-1-phenylpropanol))-*N*'-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**1i**)



Compound **1i** was obtained according to general procedure A, using (*S*)-norephedrine (1.00 g, 6.61 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 80/20 v/v). The compound was obtained as a white foamy solid (2.49 g, 5.88 mmol, 89%). m.p. 62 °C (capillary); R_f (cyclohexane/ethyl acetate, 80:20) = 0.25; $[\alpha]^{20}_D = -100.7$ (c = 0.5, $CHCl_3$);

^{1}H NMR (250 MHz, $CDCl_3$): δ = 9.49 (br s, 1H, NH), 8.37 (s, 2H, H_{Ar}), 7.84–7.58 (m, 2H, 1 × NH, 1 × H_{Ar}), 7.54–7.44 (m, 2H, H_{Ar}), 7.41–7.31 (m, 2H, H_{Ar}), 7.30–7.20 (m, 1H, H_{Ar}), 5.23–5.11 (m, 1H, CH), 4.93–4.60 (m, 2H, 1 × OH, 1 × CH), 1.06 (d, *J* = 7.0 Hz, 3H, CH_3) ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 182.3 (C=S), 144.4 (C_{Ar}), 143.9 (C_{Ar}), 132.9 (q, *J* = 32.3 Hz, 2C, CCF_3), 129.8 (2C, CH_{Ar}), 128.8 (CH_{Ar}), 127.7 (2C, CH_{Ar}), 125.6 (q, *J* = 271.6 Hz, 2C, CF_3), 124.1 (2C, CH_{Ar}), 118.6–118.1 (m, 1C, CH_{Ar}), 75.6 (CH), 57.5 (CH), 13.5 (CH_3) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* = –62.9 (m, 6F, CF_3) ppm; FTIR (Platinum ATR): $\tilde{\nu}$ = 3244 (vw), 3066 (vw), 2115 (vw), 1527 (vw), 1470 (vw), 1455 (vw), 1379 (w), 1273 (w), 1171 (w), 1125 (m), 1001 (vw), 885 (w), 847 (vw), 755 (vw), 699 (w), 679 (w), 617 (vw), 573 (vw), 531 (vw) cm^{-1}; MS (FAB), m/z (%): 423.0 (100) $[M + H]^+$, 405.0 (20) $[M - OH]^+$, 289.6 (50) $[C_9H_7F_6N_2S]^+$, 135.8 (35) $[C_9H_{11}O]^+$; HR-FABMS calcd for $C_{18}H_{17}F_6N_2OS$: 423.0965, found 423.0963 $[M + H]^+$.

Synthesis of *N*-((*R*)-(2-amino-2-phenylethanol))-*N*'-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**1j**)

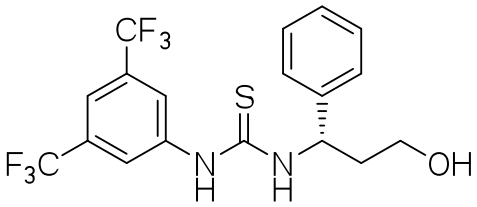


Compound **1j** was obtained according to general procedure A, using *R*-(-)-phenylglycinol (800 mg, 5.8 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 80/20 to 60/40 v/v). The compound was obtained as a white foamy solid (2.16 g, 5.28 mmol, 91%). m.p. 59 °C (capillary); R_f (cyclohexane/ethyl acetate, 80:20) = 0.21; $[\alpha]^{20}_D$ = 26.6 (c = 0.5, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67 (br s, 1H, NH), 7.70 (s, 2H, H_{Ar}), 7.55 (s, 1H, H_{Ar}), 7.48–7.43 (m, 1H, CH), 7.29–7.17 (m, 5H, H_{Ar}), 5.54 (br s, 1H, OH), 3.94–3.76 (m, 2H, CH_2), 2.79 (br s, 1H, NH) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.8 (C=S), 139.4 (CH_{Ar}), 137.2 (C_{Ar}), 132.3 (q, *J* =34.5 Hz, 2C, CCF_3), 129.2 (CH_{Ar}), 128.5 (C_{Ar}), 126.6 (4C, CH_{Ar}), 123.6 (CH_{Ar}), 122.8 (q, *J* =272.9 Hz, 2C, CF_3), 119.1–118.8 (m, CH_{Ar}), 66.0 (CH_2), 60.3 (CH) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* = –63.0 (m, 6F, CF_3) ppm; FTIR (Platinum ATR): $\tilde{\nu}$= 3259 (vw), 3067 (vw), 1667 (vw), 1529 (vw), 1470 (vw), 1380 (w), 1342 (vw), 1273 (w), 1170 (w), 1123 (w), 1060 (vw), 1001 (vw), 976 (vw), 955 (vw), 885 (vw), 847 (vw), 748 (vw), 697 (w), 679 (w), 593 (vw), 528 (vw), 401 (vw) cm^{-1}; MS (FAB), m/z (%): 409.0 (100) $[M + H]^+$, 390.0 (20) $[M - H_2O]^+$, 288.7 (10) $[C_9H_7F_6N_2S]^+$, 122.0 (25); HR-FABMS calcd for $C_{17}H_{15}F_6N_2OS$: 409.0809, found 409.0806 $[M + H]^+$. Analytical data is in accordance with the literature.[4]

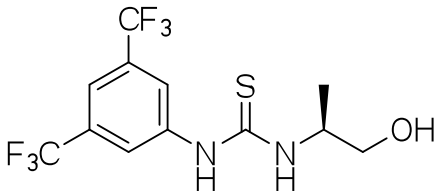
[4] Dorwald, F. Z.; Hansen, J. B.; Mogensen, J. P.; Tagmose, T. M.; Pirotte, B.; Lebrun, P.; De Tullio, P.; Boverie, S.; Delarge, J. PCT Int. Appl. (**1999**), 48 pp. CODEN:PIXXD2; WO9907672

Synthesis of *N*-((*S*)-(3-amino-3-phenylpropanol))-*N*'-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**1k**)



Compound **1k** was obtained according to general procedure A, using (*S*)-3-amino-3-phenylpropanol (250 mg, 1.65 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 80/20 v/v). The compound was obtained as a white foamy solid (650 mg, 1.53 mmol, 93%). m.p. 56 °C (capillary); R_f (cyclohexane/ethyl acetate, 80:20) = 0.30; $[\alpha]^{20}_D$ = 65.2 (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.53 (br s, 1H, NH), 7.76 (s, 2H, H_{Ar}), 7.65 (s, 1H, H_{Ar}), 7.61 (br s, 1H, NH), 7.38–7.20 (m, 5H, H_{Ar}), 5.76 (br s, 1H, OH), 3.84–3.55 (m, 2H, CH_2), 2.87–2.63 (m, 1H, CH_2), 2.21–2.11 (m, 1H, CH), 2.05–1.88 (m, 1H, CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.0 (C=S), 139.9 (C_{Ar}), 138.9 (C_{Ar}), 132.6 (q, *J* = 36.0 Hz, 2C, CCF_3), 128.9 (2C, CH_{Ar}), 127.8 (CH_{Ar}), 126.3 (2C, CH_{Ar}), 123.7 (br s, 2C, CH_{Ar}), 122.8 (q, *J* = 275.1 Hz, 2C, CF_3), 119.2–118.9 (m, 1C, CH_{Ar}), 58.9 (CH_2), 57.2 (CH), 37.4 (CH_2) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* = –62.99 (m, 6F, CF_3) ppm; FTIR (Platinum ATR): $\tilde{\nu}$= 3279 (m), 3062 (w), 2953 (w), 1805 (vw), 1622 (w), 1535 (m), 1472 (m), 1383 (m), 1343 (m), 1279 (s), 1177 (s), 1135 (s), 1044 (w), 1001 (w), 947 (w), 888 (m), 847 (w), 754 (w), 700 (m), 681 (m), 594 (w), 535 (w), 404 (vw) cm^{-1}; MS (FAB), m/z (%): 423.1 (100) $[M + H]^+$, 389.1 (10), 289.1 (30) $[C_9H_7F_6N_2S]^+$, 135.2 (10), 105.4 (60), 91.4 (35); HR-FABMS calcd for $C_{18}H_{17}F_6N_2OS$: 423.0965, found 423.0962 $[M + H]^+$.

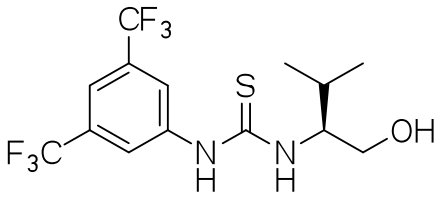
Synthesis of *N*-(2*S*)-propanol-*N*'-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**1l**)



Compound **1l** was obtained according to general procedure A, using *L*-alaninol (364 mg, 4.85 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 50/50 v/v). The compound was obtained as a white foamy solid (1.63 g, 4.70 mmol, 97%). m.p. 84 °C (capillary); R_f (cyclohexane/ethyl acetate, 70:30) = 0.16; $[\alpha]^{20}_D = -27.0$ (c = 0.5, $CHCl_3$);

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.89 (br s, 1H, NH), 7.81 (s, 2H, H_{Ar}), 7.61 (s, 1H, H_{Ar}), 7.02–6.88 (m, 1H, CH), 4.59 (br s, 1H, NH), 3.80 (dd, *J* = 10.8 Hz, *J* = 2.7 Hz, 1H, CH_2), 3.80 (dd, *J* = 10.8 Hz, *J* = 7.2 Hz, 1H, CH_2), 3.18 (br s, 1H, OH), 1.20 (d, *J* = 6.8 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.7 (C=S), 139.6 (C_{Ar}), 132.2 (q, *J* =33.0 Hz, 2C, CCF_3), 123.5 (2C, CH_{Ar}), 122.8 (q, *J* =272.9 Hz, 2C, CF_3), 118.7 (CH_{Ar}), 66.3 (CH), 52.5 (CH_2), 16.4 (CH_3) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* = –63.1 (m, 6F, CF_3) ppm; FTIR (Platinum ATR): ν̃= 3240 (vw), 3055 (vw), 1623 (vw), 1547 (w), 1468 (vw), 1381 (w), 1351 (vw), 1269 (m), 1173 (w), 1126 (m), 1046 (w), 1009 (vw), 991 (vw), 926 (vw), 888 (w), 847 (vw), 767 (vw), 743 (vw), 701 (w), 678 (w), 618 (vw), 590 (vw), 508 (vw) cm^{-1}; MS (FAB), m/z (%): 347.0 (100) $[M + H]^+$, 327.9 (30) $[M - H_2O]^+$, 312.8 (20), 288.8 (30) $[C_9H_7F_6N_2S]^+$, 136.7 (25); HR-FABMS calcd for $C_{12}H_{13}F_6N_2OS$: 347.0652, found 347.0655 $[M + H]^+$.

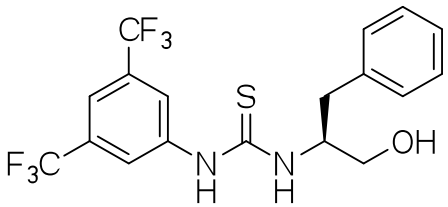
Synthesis of *N*-((*S*)-(3-methylbutanol))-*N'*-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**1m**)



Compound **1m** was obtained according to general procedure A, using (*S*)-valinol (500 mg, 4.85 mmol) as starting material. The crude product was washed with hexane and dried. The compound was obtained as a white solid (1.67 g, 4.46 mmol, 92%). m.p. 121 °C (capillary); R_f (cyclohexane/ethyl acetate, 80:20) = 0.30; $[\alpha]^{20}_D = -71.0$ (c = 0.5, $CHCl_3$);

^{1}H NMR (400 MHz, acetone-d_6): δ = 9.42 (br s, 1H, NH), 8.36 (s, 2H, H_{Ar}), 7.68 (s, 1H, H_{Ar}), 7.55 (br s, 1H, NH), 4.50–4.34 (m, 1H, CH), 3.95 (br s, 1H, OH), 3.87–3.67 (m, 1H, CH_2), 3.70–2.97 (m, 1H, CH_2), 2.16–2.07 (m, 1H, CH), 1.10 (d, *J* = 7.0 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, acetone-d_6): δ = 183.3 (C=S), 144.1 (C_{Ar}), 132.9 (q, *J* = 32.9 Hz, 2C, CCF_3), 122.8 (q, *J* = 277.3 Hz, 2C, CF_3), 124.0 (2C, CH_{Ar}), 118.1 (CH_{Ar}), 62.8 (br s, 2C, CH, CH_2), 31.0 (CH), 20.7 (CH_3), 20.3 (CH_3); ^{19}F NMR (376 MHz, $CDCl_3$): *δ* = –63.1 (m, 6F, CF_3) ppm; FTIR (KBr): $\tilde{\nu}$ = 3648 (w), 2484 (w), 3270 (m), 3049 (m), 2970 (m), 1792 (vw), 1624 (w), 1538 (m), 1468 (m), 1385 (s), 1358 (m), 1277 (s), 1185 (s), 1138 (s), 1063 (w), 983 (w), 951 (w), 926 (vw), 889 (m), 847 (w), 822 (vw), 709 (m), 681 (m), 594 (w) cm^{-1}; EI-MS m/z (%): 374.2 (15) $[M]^+$, 356.2 (38) $[M - OH]^+$, 341.1 (58) $[M - CH_3]^+$, 289.1 (100) $[M - C_5H_{11}O]^+$; HR-EIMS calcd for $C_{14}H_{16}F_6N_2O_6$: 374.0887, found: 374.0885 $[M]^+$. elemental analysis calcd (%) for $C_{14}H_{16}F_6N_2OS$: N 7.48, C 44.92, H 4.31; found: N 7.44, C 44.83, H 4.13.

Synthesis of *N*-((2*S*)-(3-phenylpropanol))-*N*'-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**1n**)

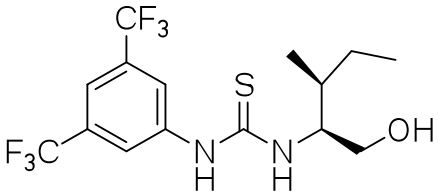


Compound **1n** was obtained according to general procedure A, using (*S*)-phenylalaninol (1.00 g, 6.61 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 70/30 v/v). The compound was obtained as a white foamy solid (2.54 g, 6.02 mmol, 91%). m.p. 102 °C (capillary); (lit.[5]: 62 °C); R_f (cyclohexane/ethyl acetate, 70:30) = 0.32; $[\alpha]^{20}_D$ = –56.8 (c = 0.5, $CHCl_3$); (lit.[5]: –54 (c = 0.3, $CHCl_3$);

^{1}H NMR (250 MHz, acetone-d_6): δ = 9.49 (br s, 1H, NH), 8.35 (s, 2H, H_{Ar}), 7.69 (s, 1H, H_{Ar}), 7.63 (br s, 1H, NH), 7.38–7.16 (m, 5H, H_{Ar}), 4.71 (br. s, 1H, OH), 4.34–4.07 (m, 1H, CH), 3.78–3.59 (m, 2H, CH_2), 3.11 (dd, *J* = 13.4 Hz, *J* = 6.1 Hz, 1H, CH_2), 2.97 (dd, *J* = 13.4 Hz, *J* = 8.2 Hz, 1H, CH_2) ppm; ^{13}C NMR (63 MHz, acetone-d_6): δ = 182.7 (C=S), 143.9 (C_{Ar}), 140.5 (C_{Ar}), 132.9 (q, *J* = 35.4 Hz, 2C, CCF_3), 131.1 (2C, CH_{Ar}), 130.2 (2C, CH_{Ar}), 128.1 (CH_{Ar}), 125.6 (q, *J* = 272.8 Hz, 2C, CF_3), 124.2 (br s, 2C, 2 × CH), 118.6–118.0 (m, 1C, CH_{Ar}), 62.9 (CH_2), 59.2 (CH_2), 38.0 (CH_3) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.98 (s, 6F, CF_3) ppm; FTIR (Platinum ATR): $\tilde{\nu}$= 3581 (m), 3481 (m), 3211 (s), 3057 (s), 2926 (m), 2876 (m), 1955 (vw), 1806 (vw), 1662 (w), 1623 (w), 1535 (s), 1470 (s), 1383 (s), 1341 (s), 1277 (vs), 1173 (vs), 1132 (vs), 1043 (m), 984 (m), 942 (w), 914 (w), 893 (s), 847 (w), 828 (vw), 752 (m), 701 (s), 681 (s), 660 (w), 638 (w), 581 (w), 506 (w), 468 (vw) cm^{-1}; MS (FAB), m/z (%): 423.1 (100) $[M + H]^+$, 404.1 (20) $[M – H_2O]^+$, 389.2 (10), 289.1 (10) $[C_9H_7F_6N_2S]^+$, 91.4 (35); HR-FABMS calcd for $C_{18}H_{17}F_6N_2OS$: 423.0965, found 423.0961 $[M + H]^+$. Analytical data is in accordance with the literature.[5]

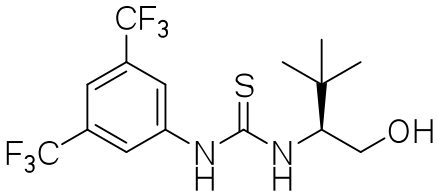
[5] Herrera, R. P.; Monge, D.; Martin-Zamora, E.; Fernandez, R.; Lassaletta, J. M. *Org. Let.* **2007**, *9*, 17, 3303.

Synthesis of *N*-((2*S*,3*S*)-(2-amino-3-methyl-pentanol))-*N*'-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**1o**)



Compound **1o** was obtained according to general procedure A, using (*S*)-isoleucinol (901 mg, 7.68 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 80/20 v/v). The compound was obtained as a white foamy solid (2.80 g, 7.19 mmol, 93%). m.p. 59 °C (capillary); R_f (cyclohexane/ethyl acetate, 70:30) = 0.28; $[\alpha]^{20}_D$ = 60.2 (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.96 (br s, 1H, OH), 7.76 (s, 2H, H_{Ar}), 7.61 (s, 1H, H_{Ar}), 6.99–6.77 (m, 1H, CH), 4.50 (br s, 1H, NH), 3.92–3.81 (m, 1H, CH_2), 3.70–3.58 (m, 1H, CH_2), 3.02 (br s, 1H, NH), 1.73–1.57 (m, 1H, CH), 1.53–1.38 (m, 1H, CH_2), 1.27–1.07 (m, 1H, CH_2), 0.94–0.85 (m, 6H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.9 (C=S), 139.2 (C_{Ar}), 132.4 (q, *J* = 35.9 Hz, 2C, CCF_3), 123.7 (br s, 2C, CH_{Ar}), 122.9 (q, *J* = 276.6 Hz, 2C, CF_3), 119.3–118.3 (m, 1C, CH_{Ar}), 62.7 (CH), 60.5 (CH_2), 36.0 (CH_2), 25.8 (CH_2), 15.4 (CH_3), 11.1 (CH_3) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): *δ* = –63.1 (m, 6F, CF_3) ppm; FTIR (Platinum ATR): $\tilde{\nu}$ = 3199 (w), 3047 (w), 2970 (w), 2883 (w), 1794 (vw), 1622 (vw), 1531 (w), 1469 (w), 1383 (m), 1346 (w), 1285 (m), 1178 (m), 1130 (m), 1109 (w), 1022 (vw), 997 (w), 972 (w), 949 (w), 891 (w), 848 (vw), 775 (vw), 704 (w), 682 (w), 589 (vw) cm^{-1}; MS (FAB), m/z (%): 389.2 (100) $[M + H]^+$, 370.2 (20) $[M - H_2O]^+$, 341.2 (10), 289.2 (20) $[C_9H_7F_6N_2S]^+$, 118.5 (10) $[C_6H_{16}NO]^+$; HR-FABMS calcd for $C_{15}H_{19}F_6N_2OS$: 389.1122, found 389.1129 $[M + H]^+$.

Synthesis of *N*-((*S*)-(2-amino-3,3-dimethylbutanol))-*N*'-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**1p**)



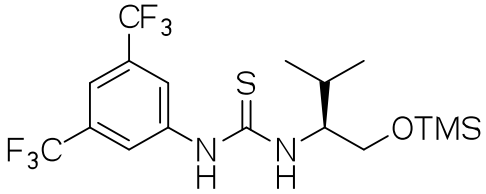
Compound **1p** was obtained according to general procedure A, using (*S*)-*tert*-leucinol (800 mg, 6.83 mmol) as starting material. The crude product was purified by column chromatography (SiO_2, cyclohexane/ethyl acetate 80/20 v/v). The compound was obtained as a white foamy solid (2.49 g, 6.40 mmol, 94%). m.p. 56 °C (capillary); R_f (cyclohexane/ethyl acetate, 80:20) = 0.34; $[\alpha]^{20}_D$ = –75.6 (c = 0.5, $CHCl_3$);

^{1}H NMR (400 MHz, acetone-d_6): δ = 9.50 (br s, 1H, OH), 8.38 (s, 2H, H_{Ar}), 7.67 (s, 1H, H_{Ar}), 7.58 (d, *J* = 7.4 Hz, 1H, NH), 4.64–4.55 (m, 1H, CH), 3.94–3.83 (m, 2H, CH_2, NH), 3.81–3.73 (m, 1H, CH_2), 1.04 (s, 9H, CH_3) ppm; ^{13}C NMR (100 MHz, acetone-d6): δ = 184.0 (C=S), 144.1 (C_{Ar}), 132.9 (q, *J* = 33.0 Hz, 2C, CCF_3), 125.4 (q, *J* = 271.9 Hz, 2C, CF_3), 123.9 (2C, CH_{Ar}), 118.1 (CH_{Ar}), 64.8 (CH), 62.9 (CH_2), 36.4 (C), 28.6 (3C, CH_3) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = –63.10 (m, 6F, CF_3) ppm; FTIR (Platinum ATR): $\tilde{\nu}$ = 3265 (vw), 2965 (vw), 1532 (w), 1471 (vw), 1379 (w), 1342 (vw), 1273 (m), 1169 (w), 1124 (m), 1042 (w), 996 (vw), 972 (vw), 885 (w), 847 (vw), 700 (w), 680 (w), 571 (vw), 401 (vw) cm^{-1}; MS (FAB), m/z (%): 389.1 (100) $[M + H]^+$, 370.1 (20), 355.1 (10), 289.1 (15) $[C_9H_7F_6N_2S]^+$; HR-FABMS calcd for $C_{15}H_{19}F_6N_2OS$: 389.1119, found 389.1122 $[M + H]^+$; elemental analysis calcd (%) for $C_{15}H_{18}F_6N_2OS$: N 7.21, C 46.39, H 4.67; found: N 6.97, C 45.97, H 4.51. Analytical data is in agreement with the literature.[6]

The catalyst *ent*-**1p** was prepared according to the same procedure starting from commercially available (*R*)-*tert*leucinol. The spectroscopic data is in accordance with the spectroscopic data of **1p**. $[\alpha]^{20}_D$ = +77.9 (c = 0.59, $CHCl_3$)

[6] Munslow, I. J.; Wade, A. R.; Deeth, R. J.; Scott, P. *Chem. Comm.* **2004**, *22*, 2596-2597.

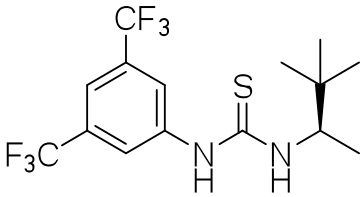
Synthesis of TMS-protected *N*-((*S*)-(3-methylbutanol))-*N'*-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**7**)



To a solution of **7** (0.10 g, 0.26 mmol, 1.00 equiv) in CH_2Cl_2 (3 mL) was added NEt_3 (0.11 mL, 0.80 mmol, 3.00 equiv) and TMSTf (0.18 g, 0.81 mmol, 3.00 equiv). The reaction was stirred for 2 h, and $NaHCO_3$ was added. The layers were separated and the combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure, to yield the title compound as a colorless oil (0.11 g, 0.25 mmol, 97%).; R_f (cyclohexane/ethyl acetate, 70:30) = 0.80; $[\alpha]^{20}_D$ = –36.6 (c = 0.5, $CHCl_3$);

^{1}H NMR (250 MHz, acetone-d_6): δ = 9.47 (br s, 1H, NH), 8.36 (s, 2H, H_{Ar}), 7.68 (s, 1H, H_{Ar}), 7.50 (br s, 1H, NH), 4.54–4.30 (m, 1H, CH), 3.87–3.68 (m, 2H, CH_2), 2.18–2.06 (m, 1H, CH), 1.00 (d, J = 7.0 Hz, 6H, CH_3), 0.12 (s, 9H, $SiMe_3$); ^{13}C NMR (63 MHz, acetone-d_6): δ = 183.2 (C=S), 144.0 (C_{Ar}), 132.9 (q, J = 32.9 Hz, 2C, CCF_3), 125.3 (q, J = 271.6 Hz, 2C, CF_3), 124.1 (2C, CH_{Ar}), 118.2 (CH_{Ar}), 63.3 (CH), 62.3 (CH_2), 48.7 (CH), 20.8 (CH_3), 20.0 (CH_3), 0.5 ($SiMe_3$); ^{19}F NMR (376 MHz, $CDCl_3$): δ = –62.9 (m, 6F, CF_3) ppm; FTIR (Platinum ATR): $\tilde{\nu}$ = 3220 (vw), 1544 (w), 1469 (w), 1382 (w), 1270 (m), 1172 (m), 1125 (m), 1104 (m), 838 (m), 678 (m) cm^{-1}; EI-MS m/z (%): 446.2 (5) $[M]^+$, 356.2 (50) $[M - OTMS]^+$, 341.1 (50) $[C_{13}H_{12}F_6N_2S]^+$, 158.1 (40), 143.1 (100); HR-EIMS calcd for $C_{17}H_{24}F_6N_2OSSi$: 446.1282, found: 446.1284 $[M]^+$.

Synthesis of *N*-((*S*)-(2-amino-3,3-dimethylbutan))-*N'*-(3,5-bis-(trifluoro-methyl)phenyl)-thiourea (**8**)



Compound **1x** was obtained according to general procedure A, using (*S*)-3,3-dimethyl-2-butylamine (1,15 g, 11.4 mmol) as starting material. The crude product was recrystallized two times from dichloromethane. The compound was obtained as a white foamy solid (4.16 g, 1.17 mmol, 98%). m.p. 156 °C (capillary); R_f (cyclohexane/ethyl acetate, 80:20) = 0.25; $[\alpha]^{20}_D = -61.3$ (c = 0.5, $CHCl_3$);

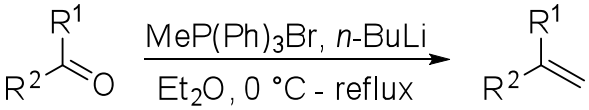
^{1}H NMR (250 MHz, acetone-d_6): δ = 9.29 (br s, 1H, NH), 8.35 (s, 2H, H_{Ar}), 7.68 (s, 1H, H_{Ar}), 7.40 (br s, 1H, NH), 4.63–4.43 (m, 1H, CH), 1.15 (d, *J* = 6.7 Hz, 3H, CH_3), 0.90 (s, 9H, CH_3) ppm; ^{13}C NMR (63 MHz, acetone-d_6): δ = 182.8 (C=S), 144.2 (C_{Ar}), 132.9 (q, *J* = 33.6 Hz, 2C, CCF_3), 125.4 (q, *J* = 272.2 Hz, 2C, CF_3), 124.0 (2C, CH_{Ar}), 118.4–117.9 (m, 1C, CH_{Ar}), 59.6 (CH), 36.3 (C), 27.7 (3C, CH_3), 16.4 (CH_3) ppm; FTIR (Platinum ATR): $\tilde{\nu}$ = 2970 (vw), 1276 (vw), 1124 (w), 888 (vw), 681 (vw) cm^{-1}; MS (FAB), m/z (%): 373.1 (100) $[M + H]^+$, 100.3 (10) $[C_6H_{14}N]^+$, 85.3 (35); HR-FABMS calcd for $C_{15}H_{19}F_6N_2S$: 373.1173, found 373.1171 $[M + H]^+$; elemental analysis calcd (%) for $C_{15}H_{18}F_6N_2S$: N 7.52, C 48.38, H 4.87, S 8.61; found: N 7.44, C 48.82, H 4.92, S 8.71.

2.2. Preparation of the substrates

Preparation of nitroalkenes

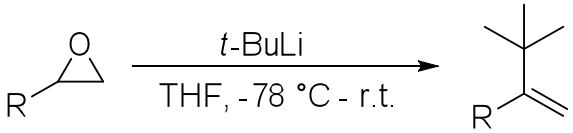
The nitroolefins were prepared according to a procedure published by *Campos et al.*[7] starting from the respective olefins. The nitroolefins were obtained by procedure C (Wittig reaction)[8] & E (olefins **2a**, **2e**-**2g**), by procedure D & E (olefin **2h**) or from commercial sources & E (olefins **2b**, **2c**, and **2d**).

Procedure C



A solution of methyltriphenylphosphonium bromide (34 mmol) in dry Et_2O (110 mL) under argon atmosphere was cooled to 0 °C and *n*-BuLi (2.5 M, 34 mmol) was added. The reaction was stirred for 3 h at this temperature and a solution of the respective ketone (37 mmol) in dry Et_2O (17 mL) was added slowly. The reaction was refluxed over night, poured into water, extracted with Et_2O (3×), dried over $MgSO_4$ and filtered. The volatiles were removed and the residue was subjected to column chromatography (cyclohexane/Et_2O 99:1 v/v) to yield the respective olefin.

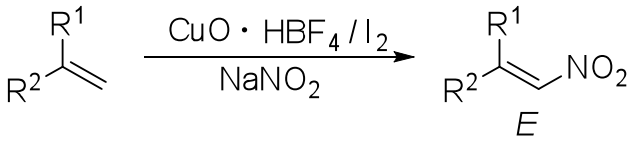
Procedure D



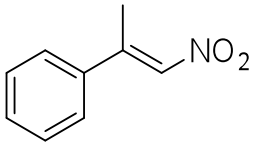
According to a procedure published by *Eisch et al.*,[9] a solution of epoxystyrene (21 mmol) in dry THF (70 mL) was cooled to -78 °C and *t*-BuLi (1.6 M in pentane, 23 mmol) was added slowly. The reaction was stirred at this temperature for 10 min and was then allowed to warm to r.t.. Water was added slowly, the layers were separated, the combined organic layer was dried over $MgSO_4$, filtered and concentrated. The resulting olefin was used without further purification.

[7] Campos, P. D.; Garcia, B.; Rodriguez, M. A. *Tetrahedron Lett.* **2000**, *41*, 979.
[8] Andrade, R. M.; Munoz, A. H.; Tamariz, J. *Synthetic Communications* **1992**, *22*, 11, 1603.
[9] Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1990**, *55*, 4835.

Procedure E

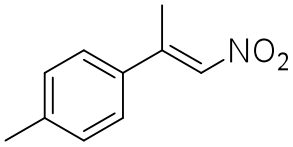


To a solution of CuO (4 mmol) in HBF_4 (35%, aqueous solution, 8 mmol), acetonitrile (20 mL) and $NaNO_2$ (24 mmol) were added respectively. After stirring for 5 min, iodine (6 mmol) and the respective olefin (20 mmol) were added. The reaction was stirred over night, water was added, and the mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed carefully with sat. $Na_2S_2O_3$, dried over $MgSO_4$, filtered and concentrated. The residue was subject to column chromatography (SiO_2, pentane/Et_2O, 99/1 – 97/3 v/v) to yield the respective *E*-nitroolefins.



(*E*)-2-Phenyl-1-nitro-1-propene (**2a**)

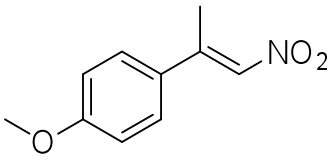
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.47–7.41 (m, 5H, H_{Ar}), 7.33–7.29 (m, 1H, $CHNO_2$), 2.65 (d, *J* = 1.53, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.8 (C), 138.2 (C, CCH_3), 136.2 (CH, $CHNO_2$), 130.2 (CH, CH_{Ar}), 128.9 (2C, CH_{Ar}), 126.7 (2C, CH_{Ar}), 18.4 (CH_3) ppm. Analytical data is in agreement with the literature.[10]



(*E*)-2-(4-Methylphenyl)-1-nitro-1-propene (**2b**)

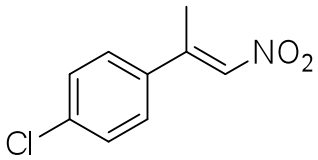
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.39–7.31 (m, 3H, 2 × H_{Ar}, $CHNO_2$), 7.25–7.16 (m, 2H, H_{Ar}), 2.63 (d, 3H, *J* = 1.2 Hz, CCH_3), 2.40 (s, 3H, Ar-CH_3) ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 150.0 (C, CCH_3), 140.9 (C, CCH_3), 135.8 (CH), 135.3 (C), 129.7 (2C, CH_{Ar}), 126.8 (2C, CH_{Ar}), 21.3 (CH_3), 18.4 (CH_3) ppm. Analytical data is in agreement with the literature.[10]

[10] Martin, N. J. A.; Ozores, L.; List, B. *J. Am. Chem. Soc*. **2007**, *129*, 8976.



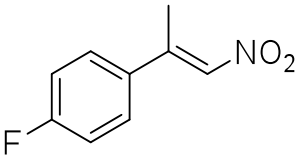
(*E*)-2-(4-Methoxyphenyl)-1-nitro-1-propene (**2c**)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.47–7.40 (m, 2H, H_{Ar}), 7.35–7.32 (m, 1H, $CHNO_2$), 6.98–6.91 (m, 2H, H_{Ar}), 3.85 (s, 3H, OCH_3), 2.64 (d, J = 1.3 Hz, 2 H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6 (C_{Ar}), 149.7 (C_{Ar}), 135.1 ($CHNO_2$), 130.2 (C), 128.4 (CH_{Ar}), 114.4 (CH_{Ar}), 55.4 (OCH_3), 18.3 (CH_3) ppm. Analytical data is in agreement with the literature.[10]



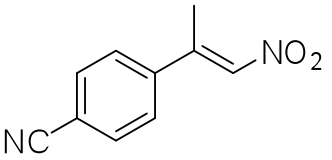
(*E*)-2-(4-Chlorophenyl)-1-nitro-1-propene (**2d**)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.45–7.36 (m, 4H, H_{Ar}), 7.28 (q, *J* = 1.4 Hz, 1H, $CHNO_2$), 2.62 (d, *J* = 1.4 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5 (C), 136.6 (C), 136.4 (CH), 129.3 (2C, CH), 129.0 (C), 128.1 (2C, CH), 18.5 (CH_3) ppm. Analytical data is in agreement with the literature.[10]



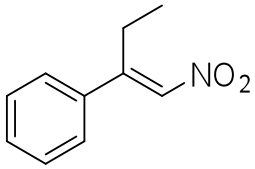
(*E*)-2-(4-Fluorophenyl)-1-nitro-1-propene (**2e**)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.49–7.41 (m, 2H, H_{Ar}), 7.29–7.26 (m, 1H, $CHNO_2$), 7.16–7.07 (m, 2H, H_{Ar}), 2.62 (d, *J* = 1.53, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.0 (d, J_{CF} = 251.6 Hz, CF), 148.7 (CCH_3), 136.2 ($CHNO_2$), 134.3 (d, J_{CF} = 3.5 Hz, C, C_{Ar}), 128.8 (d, 2C, J_{CF} = 8.7 Hz, CH_{Ar}), 116.2 (d, 2C, J_{CF} = 21.8 Hz, CH_{Ar}), 18.6 (CH_3) ppm.
Analytical data is in agreement with the literature.[10]



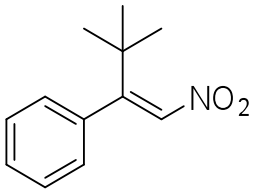
(*E*)-2-(4-Cyanophenyl)-1-nitro-1-propene (**2f**)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.81–7.72 (m, 2H, H_{Ar}), 7.59–7.52 (m, 2H, H_{Ar}), 7.29–7.27 (m, 1H, $CHNO_2$), 2.63 (d, *J* = 1.53, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.3 (C), 142.7 (C, CCH_3), 137.6 (CH, $CHNO_2$), 132.7 (2C, CH_{Ar}), 127.5 (2C, CH_{Ar}), 117.9 (CN), 113.9 (CCN), 18.3 (CH_3) ppm. Analytical data is in agreement with the literature.[10]



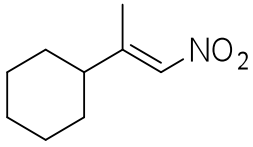
(*E*)-2-Phenyl-1-nitro-1-butene (**2g**)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.48–7.38 (m, 5H, H_{Ar}), 7.19 (s, 1H, $CHNO_2$), 3.09 (q, *J* = 7.6 Hz, 2H, CH_2), 1.16 (t, *J* =7.5 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.6 ($CHNO_2$), 136.9 (C), 135.6 (C), 130.1 (CH), 128.9 (2C, CH), 127.0 (2C, CH), 24.6 (CH_2), 12.6 (CH_3) ppm. Analytical data is in agreement with the literature.[10]



(*E*)-3,3-Dimethyl-2-phenyl-1-nitro-1-butene (**2h**)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.41–7.32 (m, 3H, H_{Ar}), 7.13–7.11 (m, 1H, $CHNO_2$), 7.09–7.02 (m, 2H, H_{Ar}), 1.18 (s, 9H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2 (C), 135.4 (CH_{Ar}), 134.7 (C_{Ar}), 127.8 (2C, CH_{Ar}), 127.7 ($CHNO_2$), 127.4 (2C, CH_{Ar}), 36.6 (CCH_3), 28.6 (3C, CH_3) ppm.



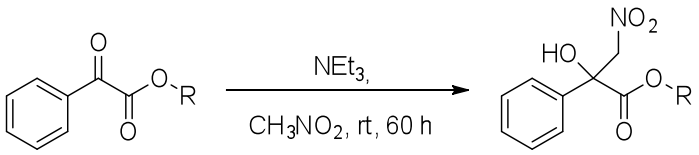
(*E*)-2-cyclohexyl-1-nitro-1-butene (**2i**)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 6.96–6.93 (m, 1H, $CHNO_2$), 2.21 (d, *J* = 1.2 Hz, 3H, CH_3), 1.89–1.65 (m, 5H, Cy), 1.60–1.55 (m, 1H, Cy), 1.35–1.17 (m, 5H, Cy) ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 157.7 (C, CCH_3), 134.8 (CH, $CHNO_2$), 46.5 (CH_{Cy}), 30.9 (2C, CH_2), 26.1 (2C, CH_2), 25.8 (CH_2), 17.2 (CH_3) ppm.

Preparation of nitroacrylates

Nitroacrylates **5a and 5b** were obtained following procedure F and G. Nitroacrylate **5c** was obtained as indicated individually below.

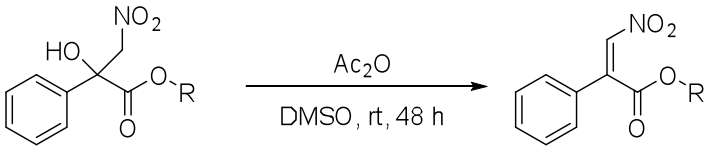
General procedure F:



Preparation of the β-nitro-α-hydroxyesters:[11]

To a solution of the β-ketoester (20 mmol) in nitromethane (80 mL) was added triethylamine (4.0 mmol). The solution was stirred for 48 h. The volatiles were removed by rotary evaporation and the residue was purified by flash chromatography to give the β-nitro-α-hydroxyesters.

General procedure G:

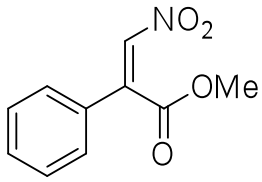


Preparation of the β-nitroacrylic ester:[12]

To a stirred solution of the respective β-nitro-α-hydroxyester (2.0 mmol) in dry DMSO (7 mL) was added Ac_2O (6.0 mmol). The reaction was stirred for 48 h. The mixture was poured into water. The two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The organic layer was washed with sat. $NaHCO_3$, dried over $MgSO_4$ and the volatiles were removed by rotary evaporation. The crude product was purified by flash chromatography to afford the β-nitroacrylic esters.

[11] Christensen, C.; Juhl, K.; Hazell, R. G.; Jørgensen, K. A. *J. Org. Chem.* **2002**, *67*, 4875-4881.
[12] Martin, J. A.; Cheng, X.; List, B. *J. Am. Chem. Soc.* **2008**, *130*, 13862.

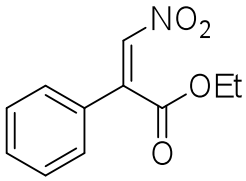
Preparation of (*Z*)-methyl 3-nitro-2-phenylacrylate (**5a**):



Starting from methylbenzoylformate, the corresponding β-nitro-α-hydroxyester was synthesized according to general procedure A. The product was purified by flash chromatography (cyclohexane/ethylacetate 90/10) (65% yield). The β-nitro-α-hydroxyester was converted into the β-nitroacrylic ester following the general procedure B. The product was purified by flash chromatography (cyclohexane/ethylacetate 95/5) (66% yield).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.52–7.46 (m, 5H, H_{Ar}), 7.36 (s, 1H, $CHNO_2$), 3.99 (s, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3 (C=O), 143.1 (C), 134.6 (CH), 132.2 (CH), 129.5 (2C, CH), 129.3 (C), 127.5 (2C, CH), 53.4 (CH_3) ppm. Analytical data is in agreement with the literature.[12]

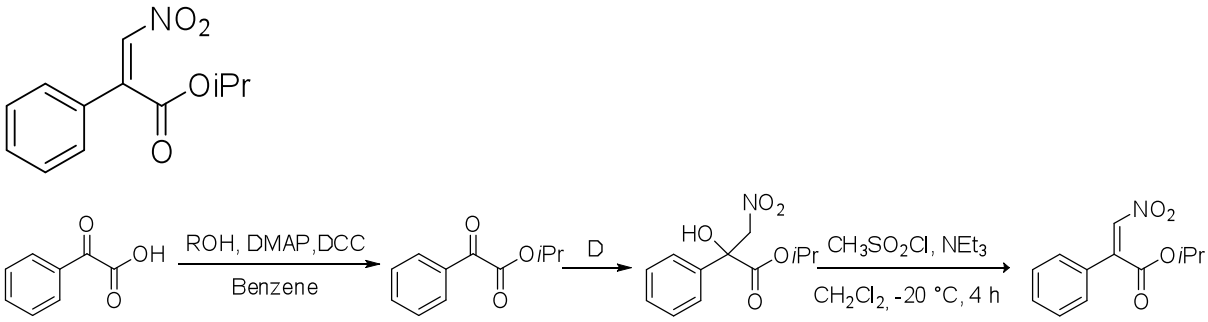
Preparation of (*Z*)-ethyl 3-nitro-2-phenylacrylate (**5b**):



Starting from ethylbenzoylformate (18.3 mmol) the corresponding β-nitro-α-hydroxyester was synthesized according to general procedure A. The product was purified by flash chromatography (cyclohexane/ethylacetate 90/10) (80% yield). The β-nitro-α-hydroxyester was converted into the β-nitroacrylic ester following thegeneral procedure B. The product was purified by flash chromatography (pentane/ether 98/2) (40% yield).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.54–7.47 (m, 5H, H_{Ar}), 7.36 (s, 1H, $CHNO_2$), 4.85 (q, *J* = 7.2 Hz, 2H, CH_2), 1.40 (t, *J* = 7.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7 (C=O), 143.3 (C), 134.4 (CH), 132.1 (CH), 129.5 (2C, CH), 128.4 (C), 127.5 (2C, CH), 62.8 (CH_2), 13.9 (CH_3) ppm. Analytical data is in agreement with the literature. [12]

Preparation of (*Z*)-Isopropyl 3-nitro-2-phenylacrylate (**5c**):[13,14]



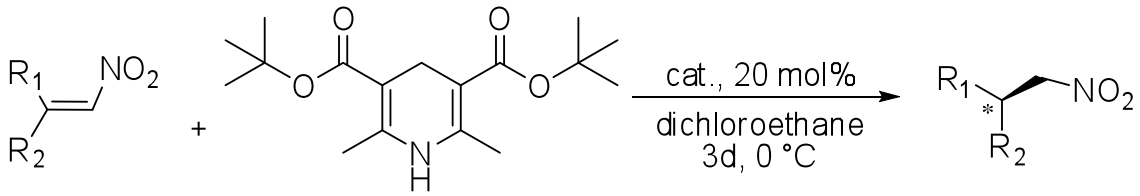
To a solution of 2-oxo-2-phenylacetic acid (25.6 mmol) in benzene (60 mL) at 0 °C was added DMAP (2.68 mmol), DCC (25.6 mmol) and isopropanol (50 mmol). The solution was stirred for 12 h at r.t. and then filtered through a plug of celite. The filtrate was concentrated and the obtained isopropyl 2-oxo-2-phenylacetate was directly used according to procedure A. The product was purified by flash chromatography (cyclohexane/ethylacetate 95/5) (80% yield). To a solution of the β-nitro-α-hydroxyester (20.0 mmol) in CH_2Cl_2 (100 mL) was added $MeSO_2Cl$ (60.0 mmol) and triethylamine (60.0 mmol) respectively. The solution was stirred for 24 h and the poured into ice water. The two layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was washed with a 15% NaOH solution, water and brine and dried over $MgSO_4$. After filtration the volatiles were removed by rotary evaporation and the crude product was purified by flash chromatography (pentane/ether 98/2) to afford the title compound in 82% yield. Analytical data is in agreement with the literature.[12]

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.53–7.46 (m, 5H, H_{Ar}), 7.34 (s, 1H, $CHNO_2$), 5.38 (sept., *J* = 6.3 Hz, 1H, C<u>H</u>$(CH_3)_2$) 1.39 (d, *J* = 6.3 Hz, 6H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.2 (C=O), 143.4 (C), 134.2 (CH), 132.0 (CH), 129.7 (C), 129.5 (2C, CH), 127.4 (2C, CH), 70.9 (CH), 21.5 (2C, CH_3) ppm. Analytical data is in agreement with the literature.[12]

[13] Hu, S.; Neckers, D. C. *J. Org. Chem.* **1996**, *61*, 6407-6415.
[14] Jayakanthan, K.; Madhusudanan, K. P.; Vankar, Y. D. *Tetrahedron* **2004**, *60*, 397-403.

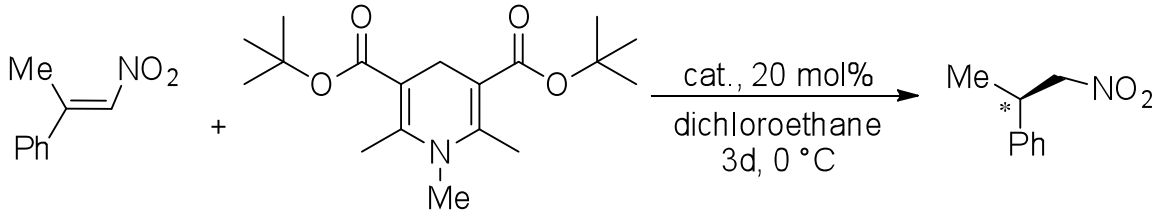
2.3. Asymmetric transferhydrogenation of nitroolefins and nitroacrylates

The asymmetric transferhydrogenation was performed following a modified procedure published by List et al..[15]



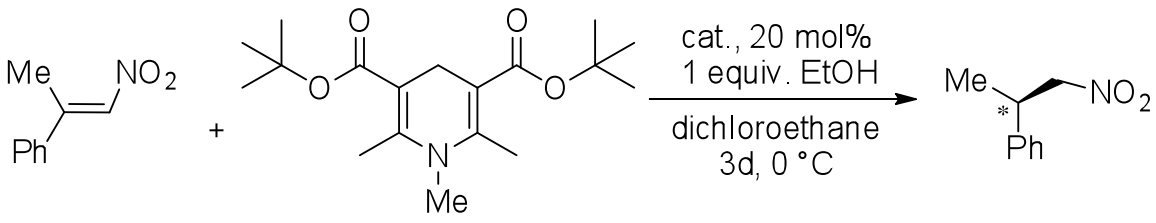
A solution of the respective nitroolefin or nitroacrylate (0.3 mmol) in 1,2-dichloroethane (0.3 mL) was cooled to 0 °C and the compound (0.06 mmol) and *t*-Bu-Hantzschester (**3**) (0.36 mmol) were added respectively. The reaction was stirred at 0 °C for 3 d. The mixture was diluted with pentane/Et_2O (99/1 v/v, 0.7 mL) and was directly subjected to column chromatography (pentane/Et_2O 99/1 - 98/2 v/v for nitroalkanes and 95/5 v/v for esters). Yields were obtained based on isolated material, except for compound **4i** (2-(Cyclohexyl)-1-nitropropane) (yield determined by GC analysis, using dodecane as internal standard).

The mechanistic studies of the asymmetric transferhydrogenation were performed according to the following procedures.



A solution of the (*E*)-2-phenyl-1-nitro-1-propene (**2a**) (0.3 mmol) in 1,2-dichloroethane (0.3 mL) was cooled to 0 °C and the catalyst **8** (0.06 mmol) and Hantzschester (**9**) (0.36 mmol) were added respectively. The reaction was stirred at 0 °C for 3 d. The mixture was diluted with pentane/Et_2O (99/1 v/v, 0.7 mL) and was directly subjected to column chromatography (pentane/Et_2O 99/1 - 98/2 v/v). Yields were determined by GC analysis, using dodecane as internal standard.

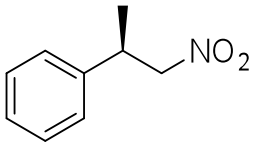
[15] Martin, N. J. A.; Ozores, L.; List, B. *J. Am. Chem. Soc.* **2007**, *129*, 8976.



A solution of the (*E*)-2-phenyl-1-nitro-1-propene (**2a**) (0.3 mmol) in 1,2-dichloroethane (0.3 mL) was cooled to 0 °C and the catalyst **8** (0.06 mmol), Hantzschester (**9**) (0.36 mmol) and Ethanol (0.3 mmol) were added respectively. The reaction was stirred at 0 °C for 3 d. The mixture was diluted with pentane/Et_2O (99/1 v/v, 0.7 mL) and was directly subjected to column chromatography (pentane/Et_2O 99/1 - 98/2 v/v). Yields were determined by GC analysis, using dodecane as internal standard.

Racemic material was obtained by $NaBH_4$ reduction in EtOH (3 h) at 0 °C.[16]

The absolute configuration was determined by comparison of analytical data available for substrate **4a** in the literature (HPLC spectra and optical rotation).[17] The absolute configuration of other substrates was determined in analogy.



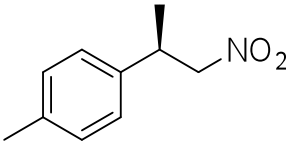
(*R*)-2-(4-Methylphenyl)-1-nitropropane (**4a**)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.45–7.23 (m, 5H, H_{Ar}), 4.63–4.46 (m, 2H, CH_2NO_2), 3.75–3.59 (m, 1H, CH), 1.42 (d, *J* = 7.0 Hz, 3H, CH_3) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.8 (C), 129.0 (2C, CH_{Ar}), 127.6 (CH_{Ar}), 126.9 (2C, CH_{Ar}), 81.9 (CH_2), 38.6 (CH), 18.7 (CH_3) ppm. Analytical data is in agreement with the literature.[10] Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak IC column (heptanes/isopropanol 99/1, 7 °C, 0.7 mL/min). Major enantiomer: t_R = 13.40 min, minor enantiomer: t_R = 14.30 min (70% *ee*).

(*S*)-2-(4-Methylphenyl)-1-nitropropane (*ent*-**4a**)

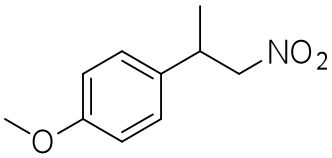
The spectroscopic data is in accordance with the data for **4a**. Minor enantiomer: t_R = 13.40 min, major enantiomer: t_R = 14.30 min (70% *ee*).

[16] Kadin, S. B. *J. Org. Chem.* **1966**, *31*, 620.
[17] Fryszkowska, A.; Fisher, K.; Gardiner, J. M.; Stephens, G. M. *J. Org. Chem.* **2008**, *73*,4295.



(*R*)-2-(4-Methylphenyl)-1-nitropropane (**4b**)

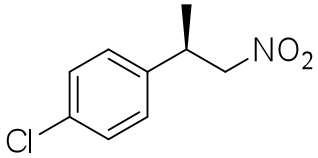
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.19–7.09 (m, 4H, H_{Ar}), 4.59–4.41 (m, 2H, CH_2), 3.69–3.52 (m, 1H, CH), 2.34 (s, 3H, Ar-CH_3), 1.37 (d, *J* = 7.3 Hz, 3H, $CHCH_3$) ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 137.8 (C, CCH), 137.2 (C, CCH_3), 129.6 (2C, CH_{Ar}), 126.7 (2C, CH_{Ar}), 81.9 (CH_2), 38.2 (CH), 21.0 (Ar-CH_3), 18.7 ($CHCH_3$) ppm. Analytical data is in agreement with the literature.[10] Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak IC column (heptanes/isopropanol 99/1, 10 °C, 0.7 mL/min). Major enantiomer: t_R = 11.31 min, minor enantiomer: t_R = 11.98 min (50% *ee*).



(*R*)-2-(4-Methoxyphenyl)-1-nitropropane (**4c**)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.18–7.11 (m, 2H, H_{Ar}), 6.92–6.83 (m, 2H, H_{Ar}), 4.58–4.39 (m, 2H, CH_2), 3.79 (s, 3 H, OCH_3), 3.66–3.52 (m, 1H, CH), 1.36 (d, *J* = 7.0 Hz, 3 H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9 (C_{Ar}), 132.8 (C_{Ar}), 127.9 (CH_{Ar}), 114.3 (CH_{Ar}), 82.1 (CH_2NO_2), 55.3 (OCH_3), 37.4 (CH), 18.8 (CH_3) ppm.

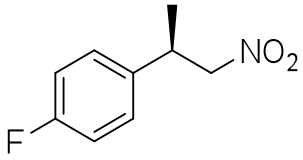
Analytical data is in agreement with the literature.[10] Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak OD column (heptanes/isopropanol 90/10, 7 °C, 0.7 mL/min). Minor enantiomer: t_R = 10.35 min, major enantiomer: t_R = 17.47 min (62% *ee*).



(*R*)-2-(4-Chlorophenyl)-1-nitropropane (**4d**)

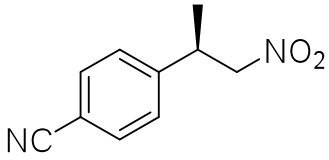
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.33–7.28 (m, 2H, H_{Ar}), 7.19–7.13 (m, 2H, H_{Ar}), 4.58–4.44 (m, 2H, CH_2NO_2), 3.71–3.55 (m, 1H, CH), 1.36 (d, *J* = 6.7 Hz, 3H, CH_3) ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 139.3 (C), 133.4 (C), 129.1 (2 C, CH), 128.3 (2 C, CH), 81.6 (CH_2), 38.1

(CH), 18.7 (CH_3) ppm. Analytical data is in agreement with the literature.[10] Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak IB column (heptanes/isopropanol 99/1, 10 °C, 0.4 mL/min). Major enantiomer: t_R = 34.67 min, minor enantiomer: t_R = 29.02 min (67% *ee*).



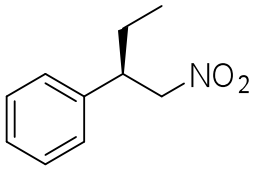
(*R*)-2-(4-Fluorophenyl)-1-nitropropane (**4e**)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.27–7.14 (m, 2H, H_{Ar}), 7.08–6.95 (m, 2H, H_{Ar}), 4.56–4.14 (m, 2H, CH_2), 3.70–3.54 (m, 1H, CH), 1.36 (d, *J* = 7.0, 3H, CH_3) ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 162.0 (d, J_{CF} = 245.9 Hz, CF), 136.5 (d, J_{CF} = 3.1 Hz, C_{Ar}), 128.4 (d, 2C, J_{CF} = 7.9 Hz, CH_{Ar}), 115.8 (d, 2C, J_{CF} = 21.4 Hz, CH_{Ar}), 81.8 (CH_2), 37.9 (CCH_3), 18.8 (CH_3) ppm. Analytical data is in agreement with the literature.[10] Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak IB column (heptanes/isopropanol 99/1, 10 °C, 0.4 mL/min). Major enantiomer: t_R = 28.65 min, minor enantiomer: t_R = 27.59 min (63% *ee*).



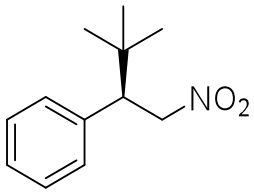
(*R*)-2-(4-Cyanophenyl)-1-nitropropane (**4f**)

^{1}H NMR (250 MHz, $CDCl_3$): δ 7.68–7.61 (m, 2H, H_{Ar}), 7.39–7.32 (m, 2H, H_{Ar}), 4.62–4.47 (m, 2H, CH_2NO_2), 3.79–3.62 (m, 1H, CH), 1.40 (d, *J* = 7.3, 3H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.2 (C), 132.8 (2C, CH_{Ar}), 127.8 (2C, CH_{Ar}), 115.3 (CN), 113.2 (CCN), 80.9 (CH_2), 38.6 (CH), 18.6 (CH_3) ppm. Analytical data is in agreement with the literature.[10] Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak IC column (heptanes/isopropanol 90/10, 15 °C, 0.7 mL/min). Major enantiomer: t_R = 46.24 min, minor enantiomer: t_R = 59.08 min (56% *ee*).



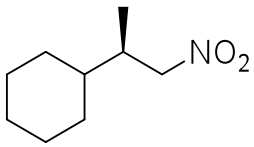
(*R*)-1-nitro-2-phenyl-butane (**4g**)

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.39–7.25 (m, 3H, H_{Ar}), 7.23–7.16 (m, 2H, H_{Ar}), 4.61–4.53 (m, 2H, CH_2NO_2), 3.44–3.30 (m, 1H, CH), 1.83–1.63 (m, 1H, CH_2CH_3), 1.83–1.63 (m, 1H, CH_2CH_3), 0.85 (t, *J* = 7.2 Hz, 1H, CH_3) ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 139.2 (C), 128.8 (2C, CH), 127.5 (3C, CH), 80.7 (CH_2NO_2), 46.0 ($CHCH_2$), 26.1 (CH_2), 11.5 (CH_3) ppm. Analytical data is in agreement with the literature.[10] Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak OD column (heptanes/isopropanol 99/1, 10 °C, 0.7 mL/min). Major enantiomer: t_R = 26.58 min, minor enantiomer: t_R = 18.74 min (68% *ee*).



(*R*)-1,1-Dimethyl-2-(4-methylphenyl)-1-nitrobutane (**4h**)

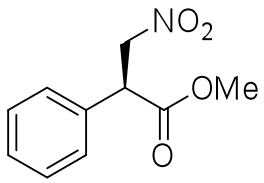
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.26–7.17 (m, 3H, H_{Ar}), 7.14–7.08 (m, 2H, H_{Ar}), 4.80–4.68 (m, 2H, CH_2NO_2), 3.30–3.25 (m, 1H, CH), 0.87 (s, 9H, CH_3) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5 (C), 129.0 (CH_{Ar}), 128.1 (2C, CH_{Ar}), 127.4 (2C, CH_{Ar}), 77.1 (CH_2NO_2), 54.3 (CH), 33.6 (CCH_3), 28.0 (3C, CH_3) ppm. Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak IB column (heptanes/isopropanol 99/1, 5 °C, 0.3 mL/min). Major enantiomer: t_R = 25.38 min, minor enantiomer: t_R = 26.55 min (87% *ee*).



(*R*)-2-(Cyclohexyl)-1-nitropropane (**4i**)

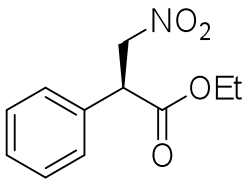
^{1}H NMR (250 MHz, $CDCl_3$): δ = 4.46–4.37 (m, 1H, CH_2NO_2), 4.23–4.10 (m, 1H, CH_2NO_2), 2.31–2.12 (m, 1H, $CHCH_3$), 1.81–1.59 (m, 5H, Cy), 1.32–1.00 (m, 6, Cy), 0.96 (d, *J* = 7.0 Hz,

3H, CH_3), ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 80.2 (CH, $CHNO_2$), 40.4 (CH, Cy), 37.7 (CH_2, Cy), 30.2 (CH_2, Cy), 28.7 (CH_2, Cy), 26.9 (CH, $CHCH_3$), 26.3 (CH_2, Cy), 26.2 (CH_2, Cy), 14.0 (CH_3) ppm. Yield determined by GC analysis using dodecane as internal standard (Zebron ZB-5MS column, 40 °C to 280 °C, ramp: 20 °C/min, R_t(dodecane) = 11.4, R_t(product) = 12.5 min). Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak IC column (heptanes/isopropanol 99/1, 10 °C, 0.7 mL/min). Major enantiomer: t_R = 10.17 min, minor enantiomer: t_R = 11.15 min (40% *ee*). The unpolarity of the compound made it impossible to obtain a clean sample for HPLC analysis by common chromatographic means. The enantiomers could clearly be determined by comparison of the respective UV spectra and comparison with racemic material.



(*R*)-Methyl 3-nitro-2-phenylpropanoate (**6a**)

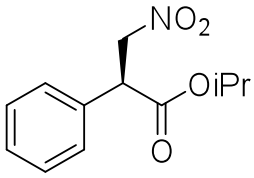
^1H NMR (250 MHz, $CDCl_3$): δ = 7.38–7.24 (m, 5H, H_{Ar}), 5.10 (dd, *J* = 14.5 Hz, *J* = 9.8 Hz, 1H, CH_2NO_2), 4.55 (dd, *J* = 14.5 Hz, *J* = 5.1 Hz, 1H, CH_2NO_2), 4.44 (dd, *J* = 9.8 Hz, *J* = 5.1 Hz, 1H, CH) 3.73 (s, 3H, CH_3) ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 170.4 (C=O), 132.5 (C), 128.7 (2C, CH), 128.0 (CH), 127.1 (2C, CH), 75.0 (CH_2), 52.2 (CH), 47.9 (CH_3) ppm. Determination of the enantiomeric excess ee was accomplished by HPLC analysis using a Chiralpak IC column (heptanes/isopropanol 99/1, 10 °C, 0.7 mL/min). Major enantiomer: t_R = 62.97 min, minor enantiomer: t_R = 36.16 min (60% ee).



(*R*)-Ethyl 3-nitro-2-phenylpropanoate (**6b**)

^1H NMR (250 MHz, $CDCl_3$): δ = 7.38–7.25 (m, 5H, H_{Ar}), 5.10 (dd, *J* = 14.6 Hz, *J* = 10.0 Hz, 1H, CH_2NO_2), 4.54 (dd, *J* = 14.6 Hz, *J* = 5.1 Hz, 1H, CH_2NO_2), 4.42 (dd, *J* = 10.0 Hz, *J* = 5.1 Hz, 1H, CH), 4.2 (m, 2H, $C\underline{H_2}CH_3$), 1.22 (t, *J* =7.1 Hz, 3H, CH_3) ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 170.5 (C=O), 133.3 (C), 129.3 (2C, CH), 128.6 (CH), 127.9 (2C, CH), 75.8 (CH_2), 61.9 (CH), 48.8 (CH_2), 13.9 (CH_3) ppm. Determination of the enantiomeric excess *ee*

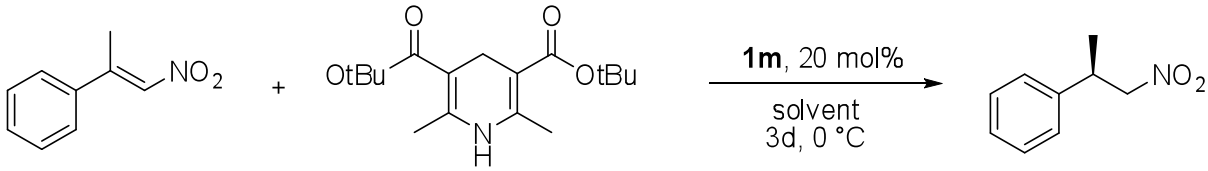
was accomplished by HPLC analysis using a Chiralpak IB column (heptanes/isopropanol 99/1, 10 °C, 0.5 mL/min). Major enantiomer: t_R = 59.24 min, minor enantiomer: t_R = 35.04 min (58% *ee*).



(*R*)-Isopropyl 3-nitro-2-phenylpropanoate (**6c**)

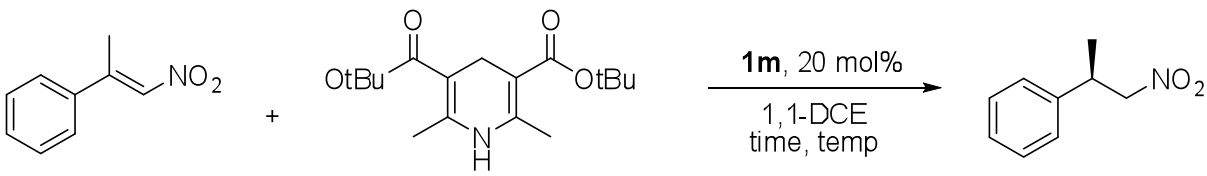
^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.36–7.20 (m, 5H, H_{Ar}), 5.12–4.92 (m, 2H, C<u>H</u>$(CH_3)_2$), CH_2NO_2), 4.50 (dd, *J* = 14.6 Hz, *J* = 5.1 Hz, 1H, CH_2NO_2), 4.37 (dd, *J* = 10.1 Hz, *J* = 5.1 Hz, 1H, CHCO), 1.25 (d, *J* = 6.3 Hz, 3H, CH_3), 1.11 (d, *J* = 6.2 Hz, 3H, CH_3) ppm; ^{13}C NMR (63 MHz, $CDCl_3$): δ = 170.2 (C=O), 133.6 (C), 129.5 (2C, CH), 128.7 (CH), 128.0 (2C, CH), 76.0 (CH_2), 69.8 (CH), 49.2 (CH), 21.8 (CH_3), 21.5 (CH_3) ppm. Determination of the enantiomeric excess *ee* was accomplished by HPLC analysis using a Chiralpak IC column (heptanes/isopropanol 99/1, 10 °C, 0.7 mL/min). Major enantiomer: t_R = 34.34 min, minor enantiomer: t_R = 19.95 min (54% *ee*).

Screening of solvents



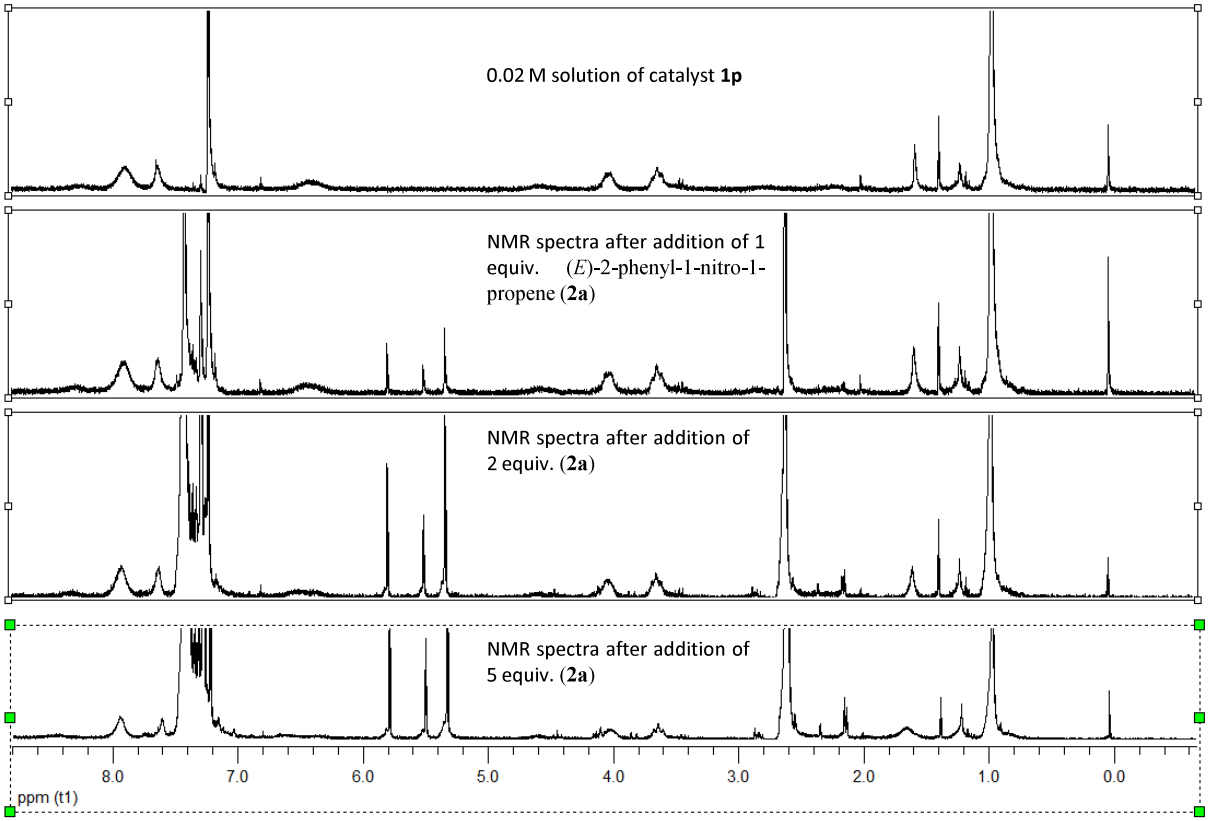
entry	solvent	yield (%)	ee (%)
1	Et_2O	54,8	77,4
2	THF	96,2	52,9
3	benzene	56,7	63,5
4	EtOAc	82,7	51,4
5	hexane	79,4	55,5
6	toluene	80	57.3
7	1,2-DCE	91,2	67,0
8	CH_2Cl_2	63	61.9
9	DMSO/DCE (1:1)	89	0

Screening of conditions



entry	time	solvent (conc)	temp	yield (%)	ee (%)
1	3d	DCE (0,1M)	0	65,9	58,4
2	3d	DCE (2M)	0	96,5	59,5
3	6d	DCE (0.5 M)	-24	40,3	56,1
4	8d	DCE (1M)	-24	68,0	60,4
5	2d	DCE (1M)	20	99	43

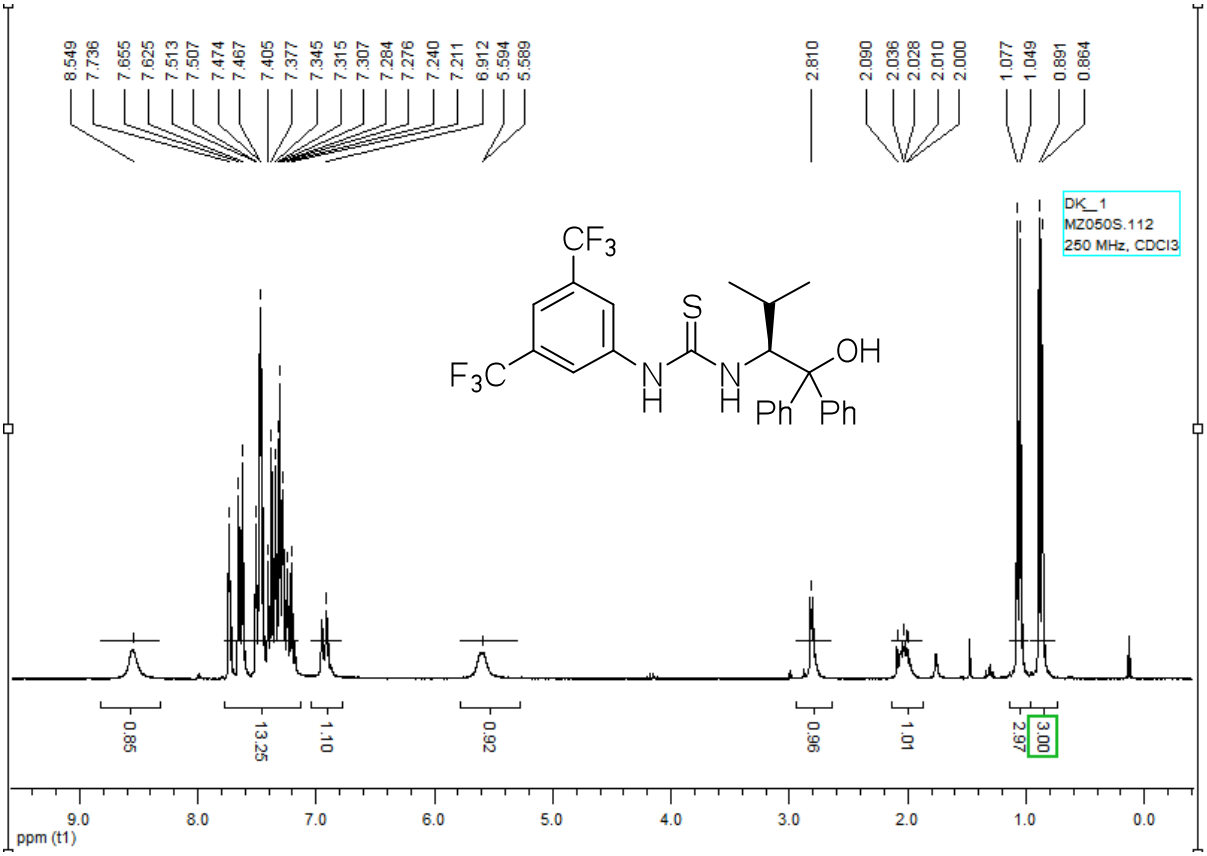
NMR spectra of catalyst **1p** with different amounts of (*E*)-2-phenyl-1-nitro-1-propene (**2a**).

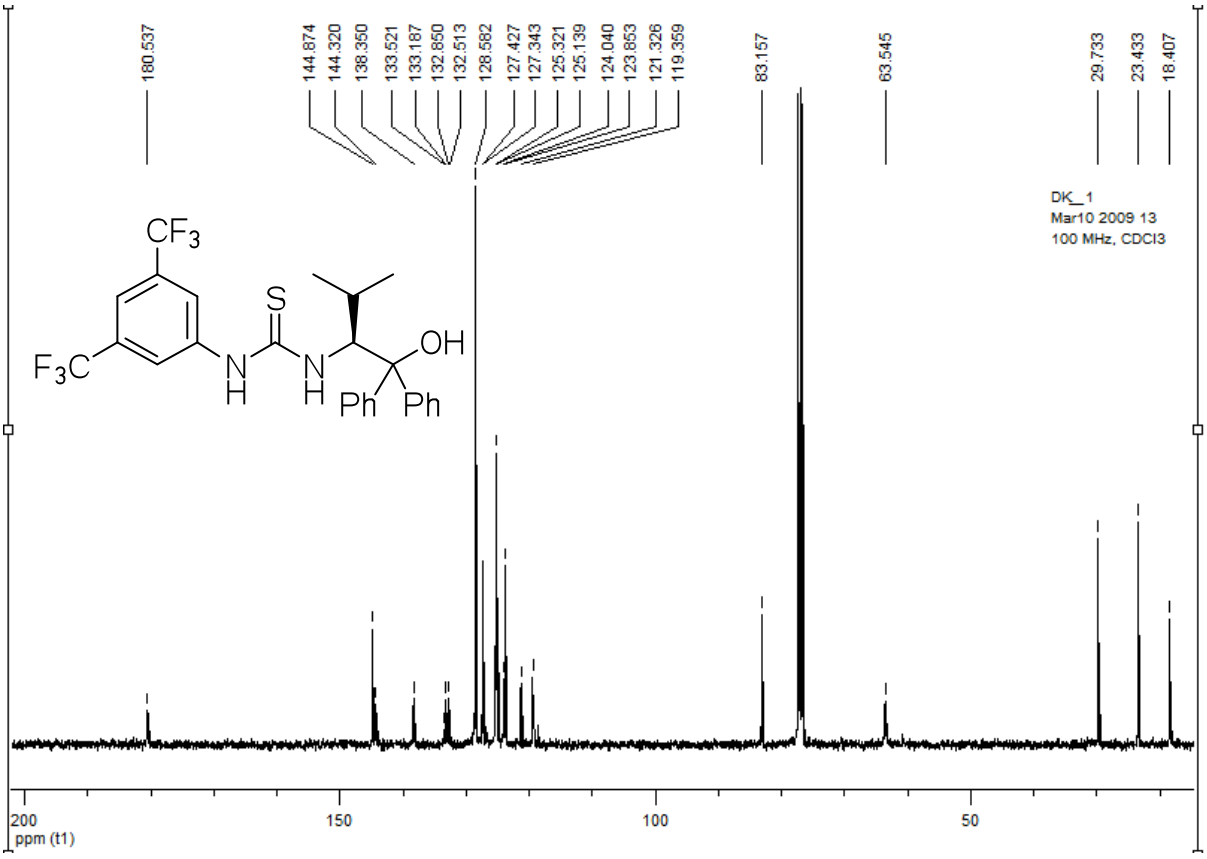


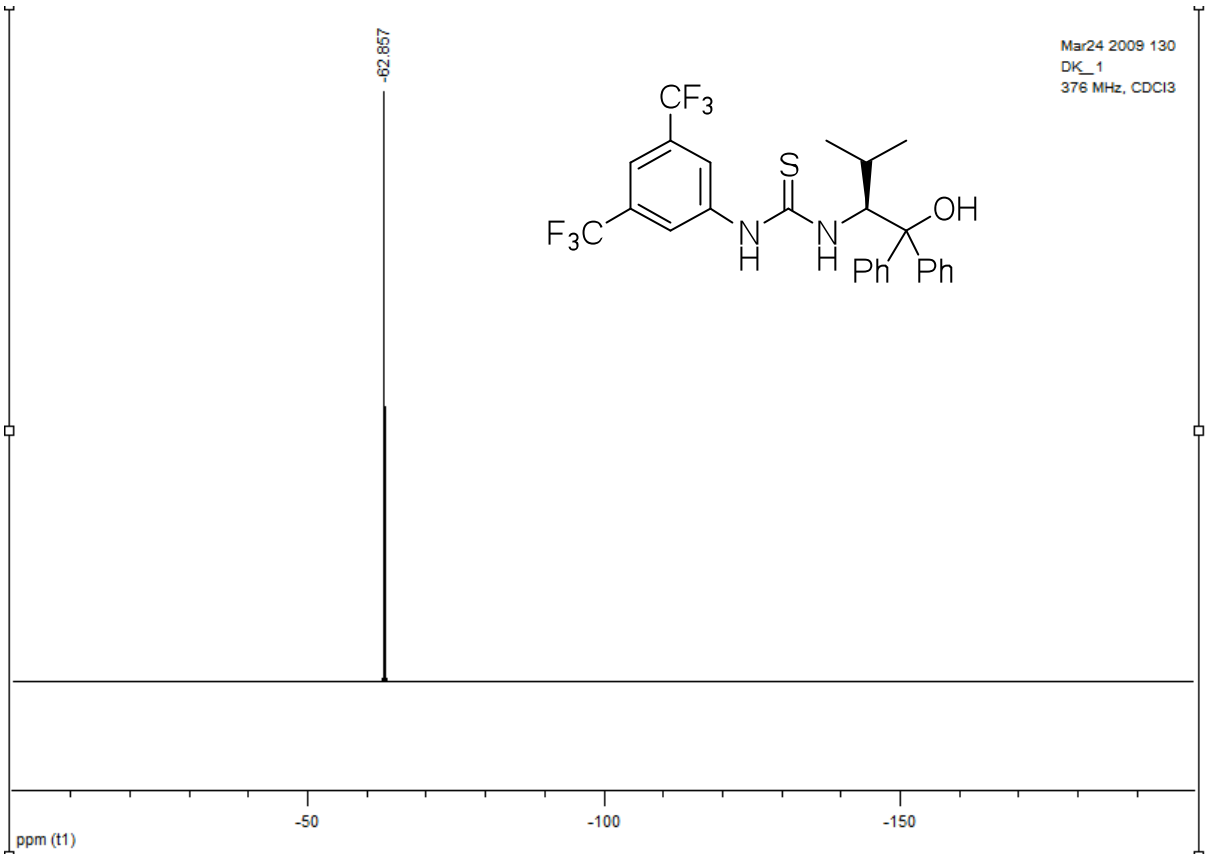
3. Spectra

3.1 NMR spectra of the catalysts

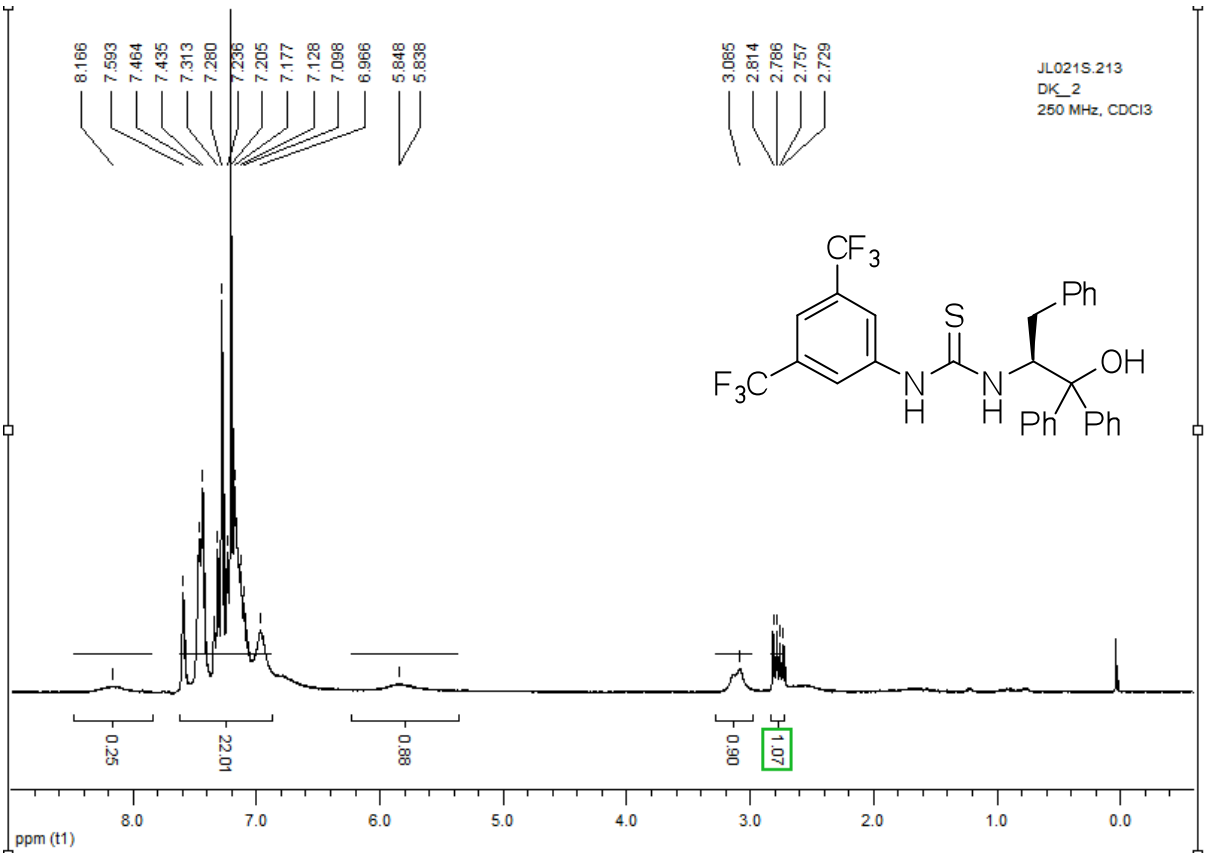
1a

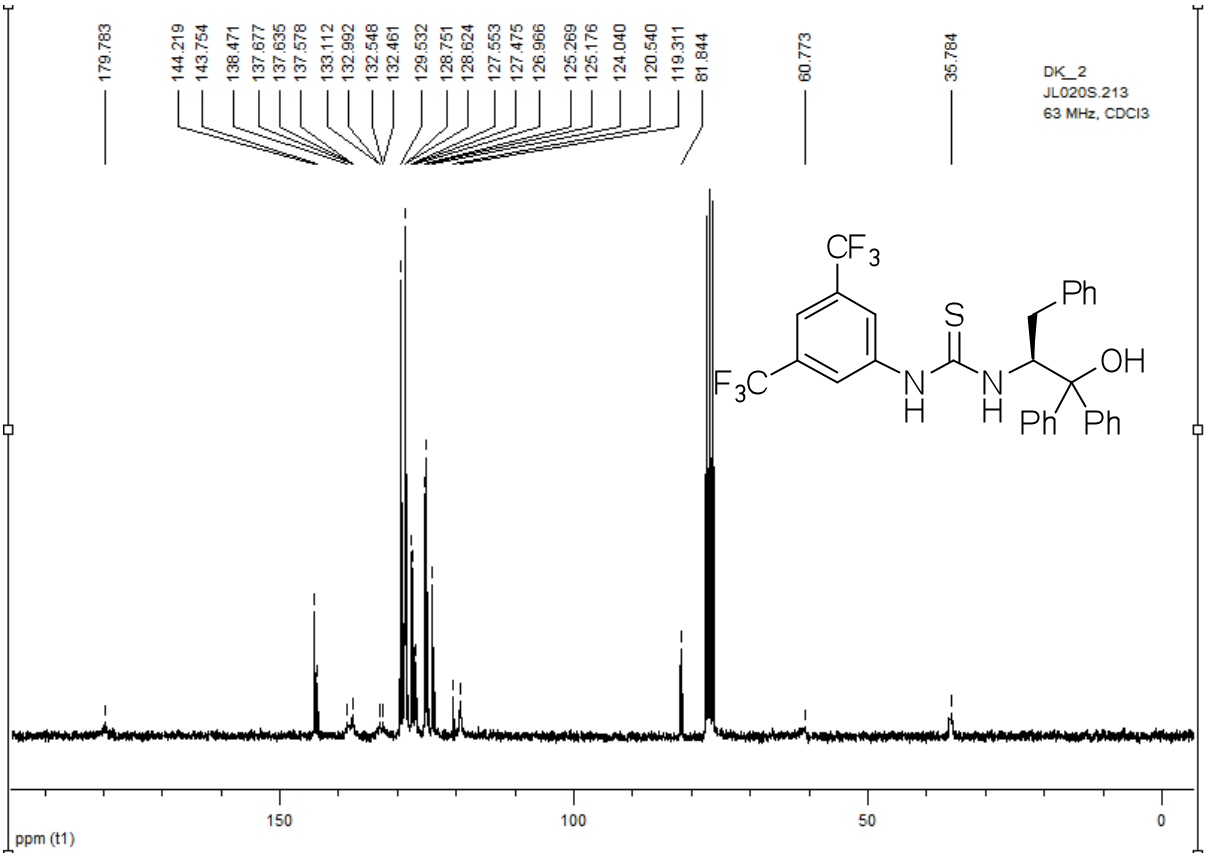


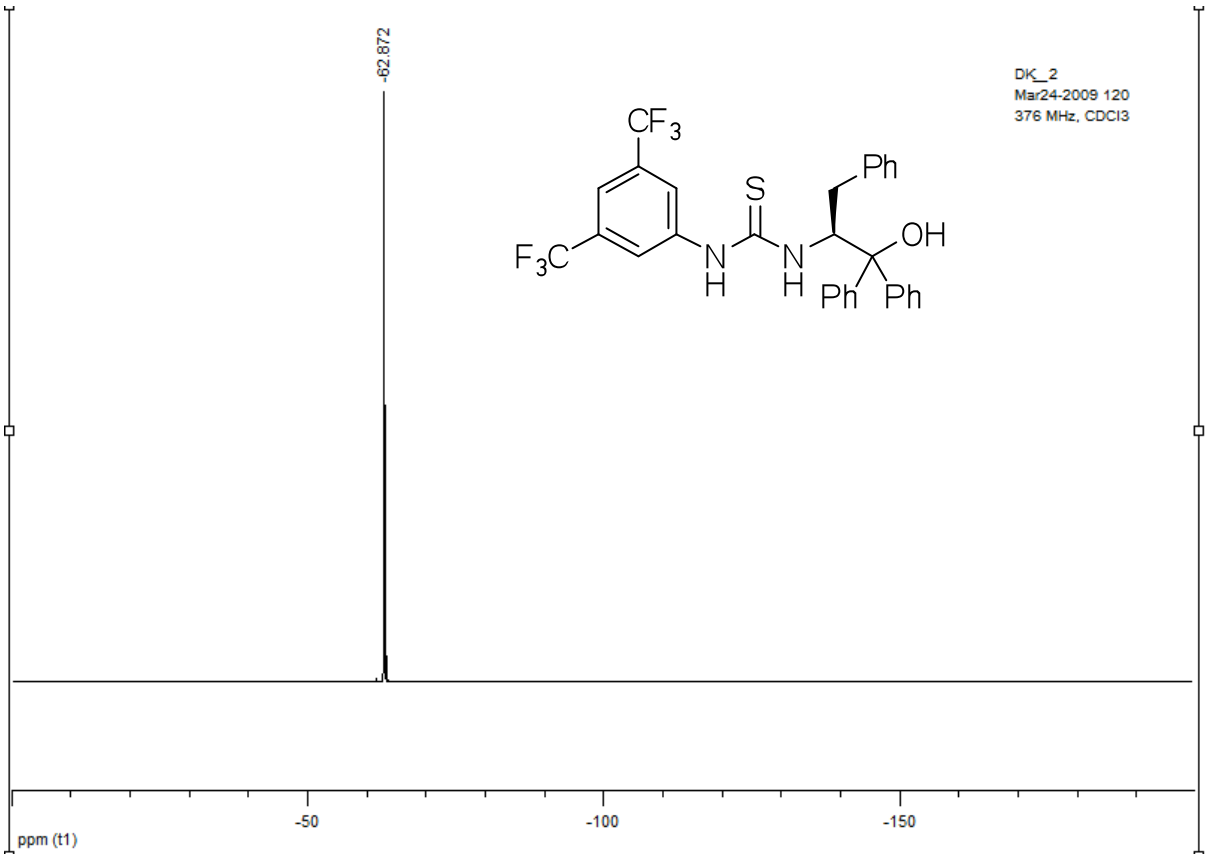




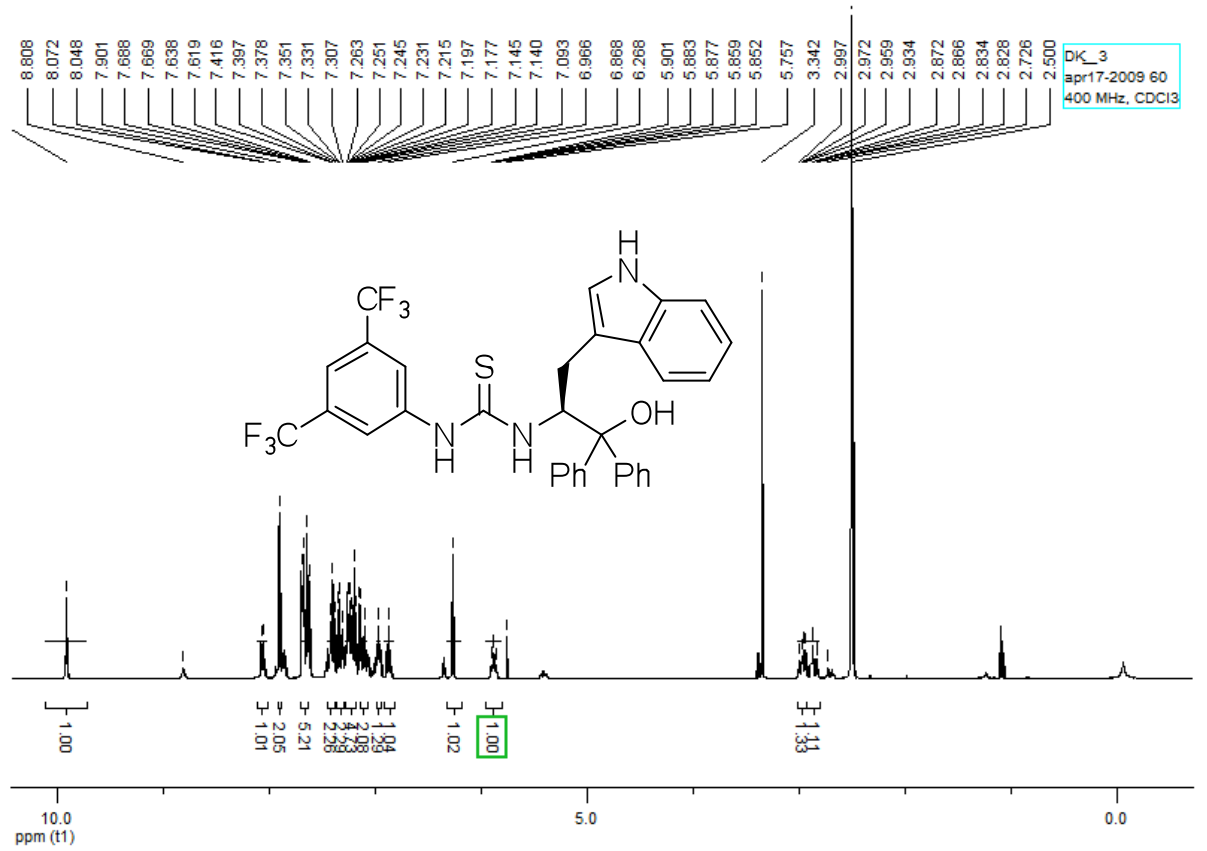
1b

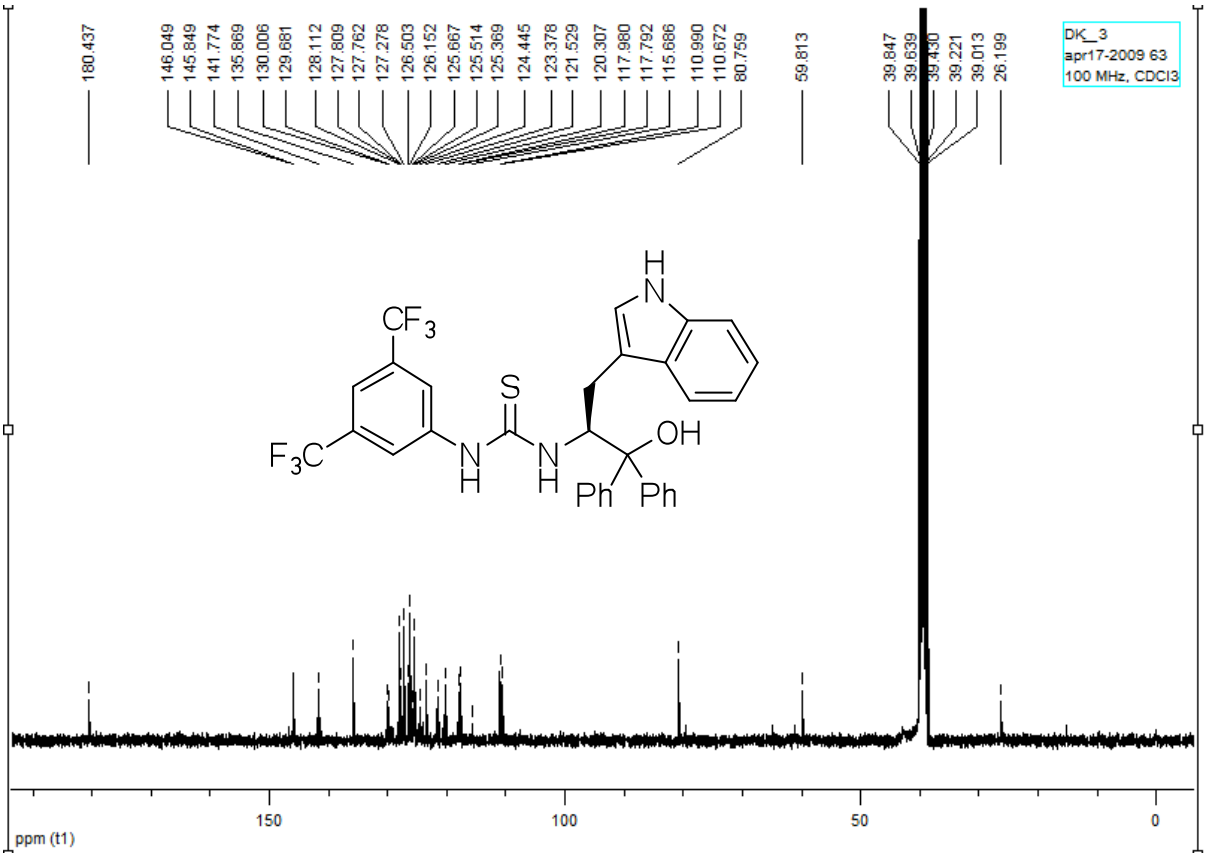

8.166
7.593
7.464
7.435
7.313
7.280
7.236
7.205
7.177
7.128
7.098
6.966
5.848
5.838
3.085
2.814
2.786
2.757
2.729
JL021S.213
DK_2
250 MHz, CDCl3
CF3
F3C
S
N
H
N
H
Ph
OH
Ph
Ph
0.25
22.01
0.88
0.90
1.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

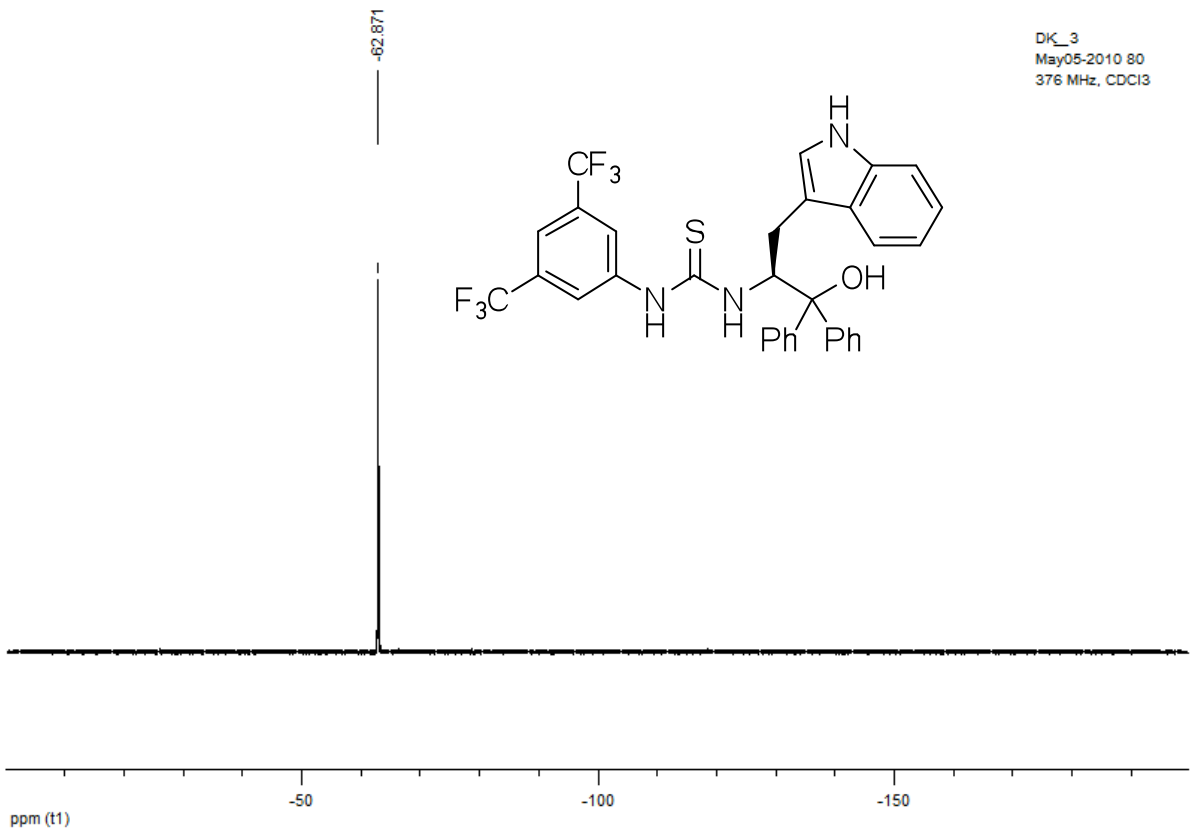

179.783
144.219
143.754
138.471
137.677
137.635
137.578
133.112
132.992
132.548
132.461
129.532
128.751
128.624
127.553
127.475
126.966
125.269
125.176
124.040
120.540
119.311
81.844
60.773
35.784
DK_2
JL020S.213
63 MHz, CDCl3
CF3
F3C
S
N
H
N
H
Ph
OH
Ph
Ph
150
100
50
0
ppm (t1)



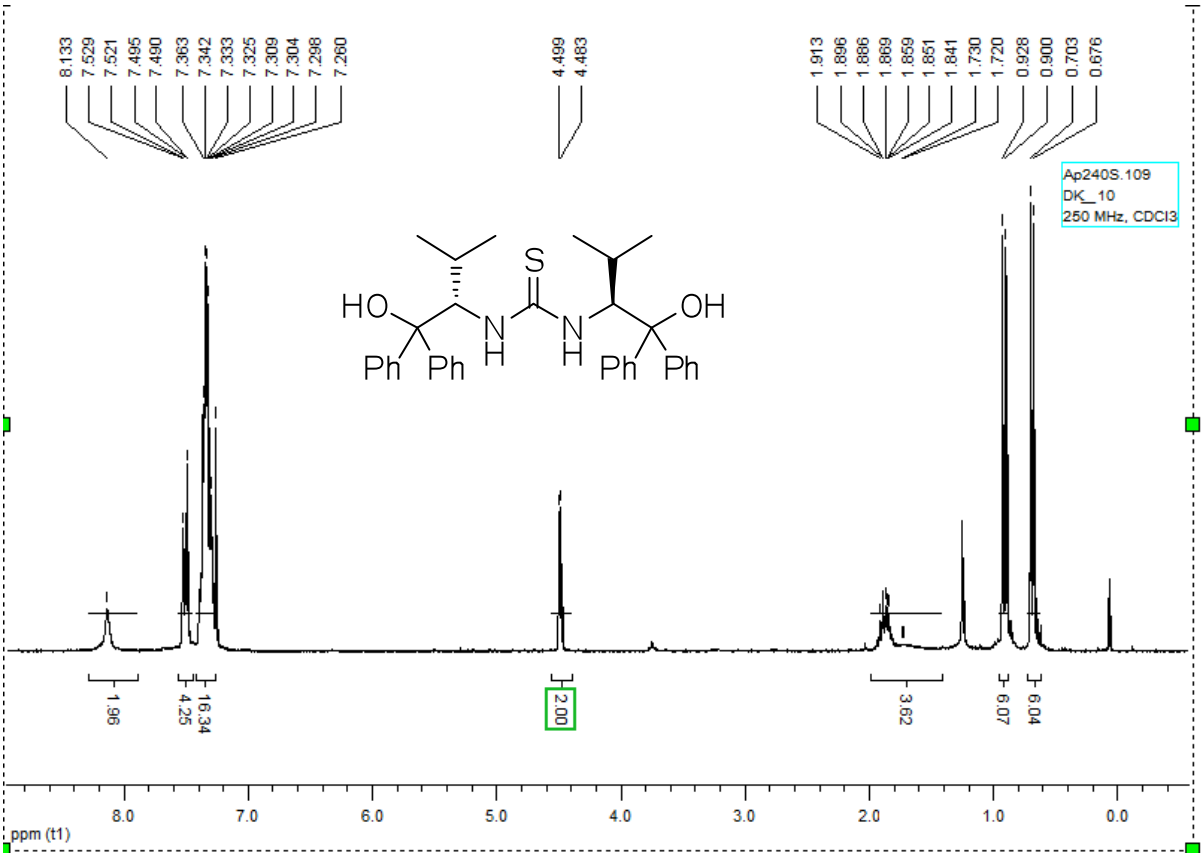
1c

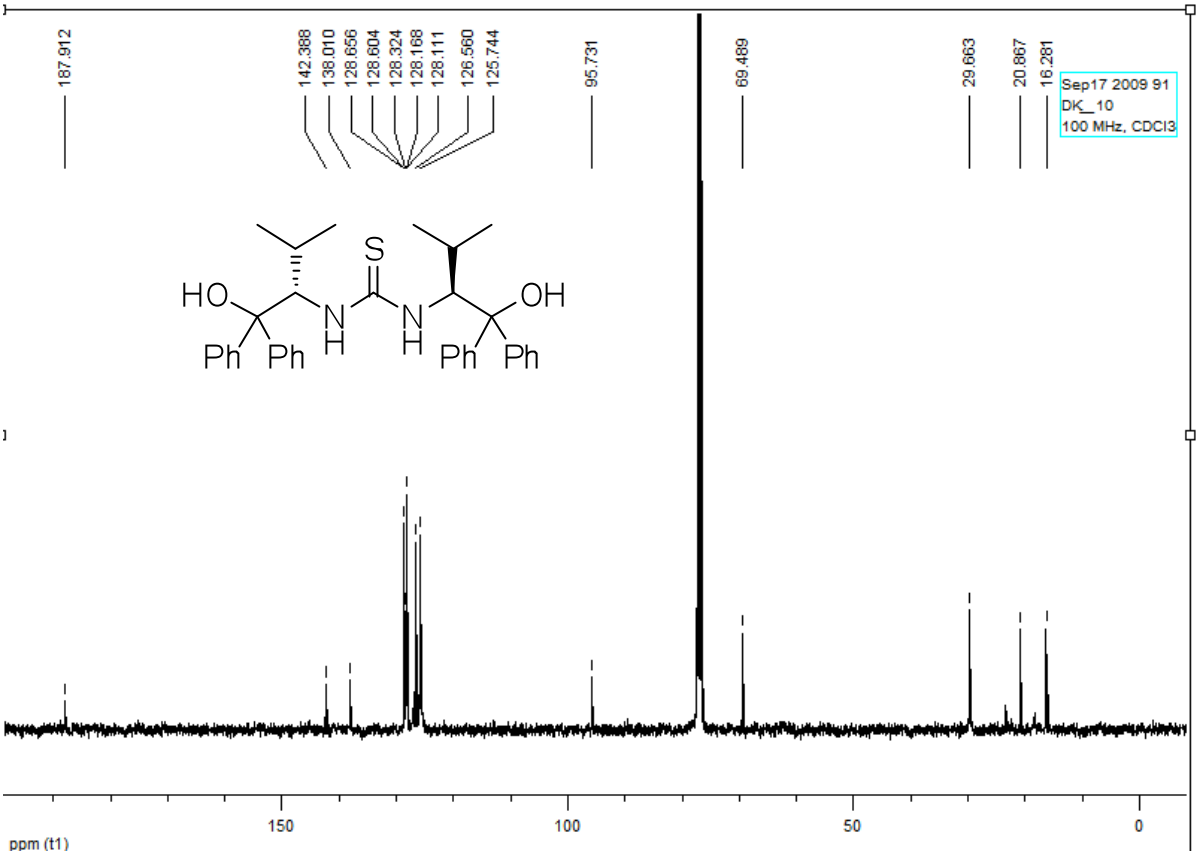

DK_3
apr17-2009 60
400 MHz, CDCl3
ppm (t1)


DK_3
apr17-2009 63
100 MHz, CDCl3
ppm (t1)

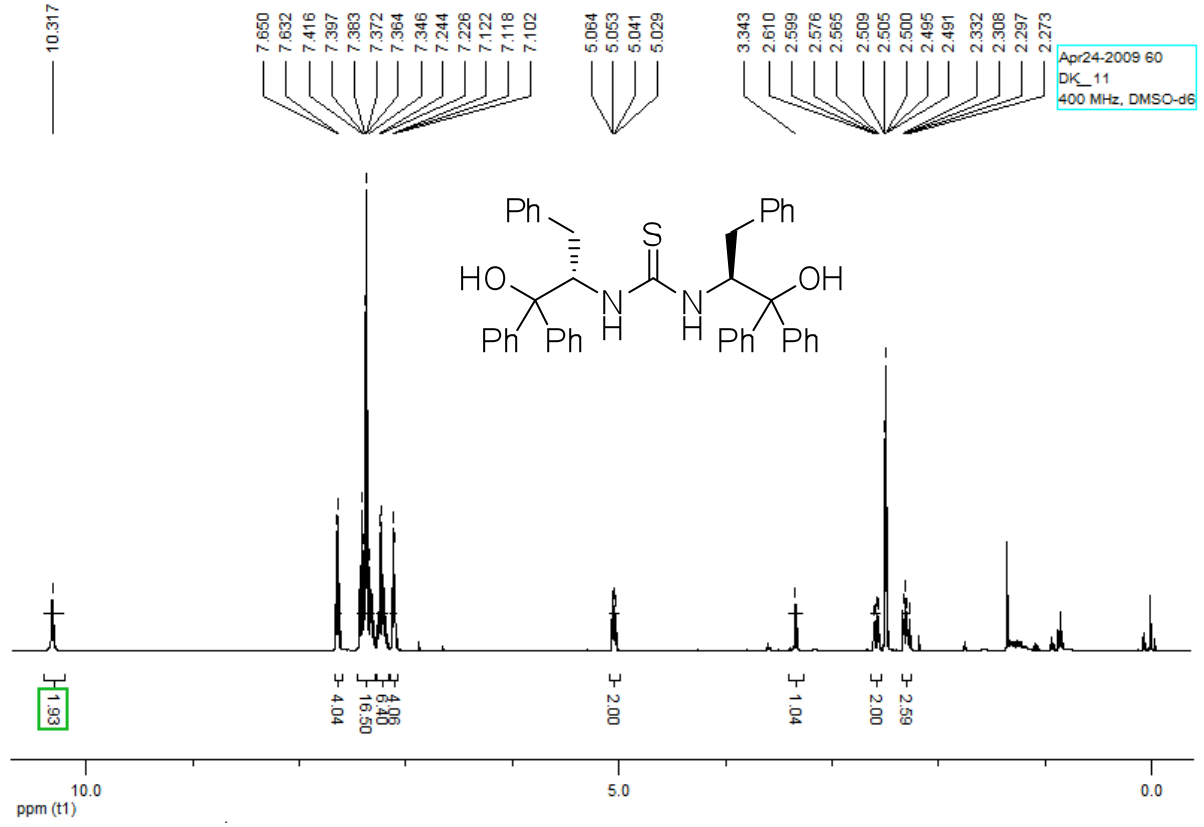


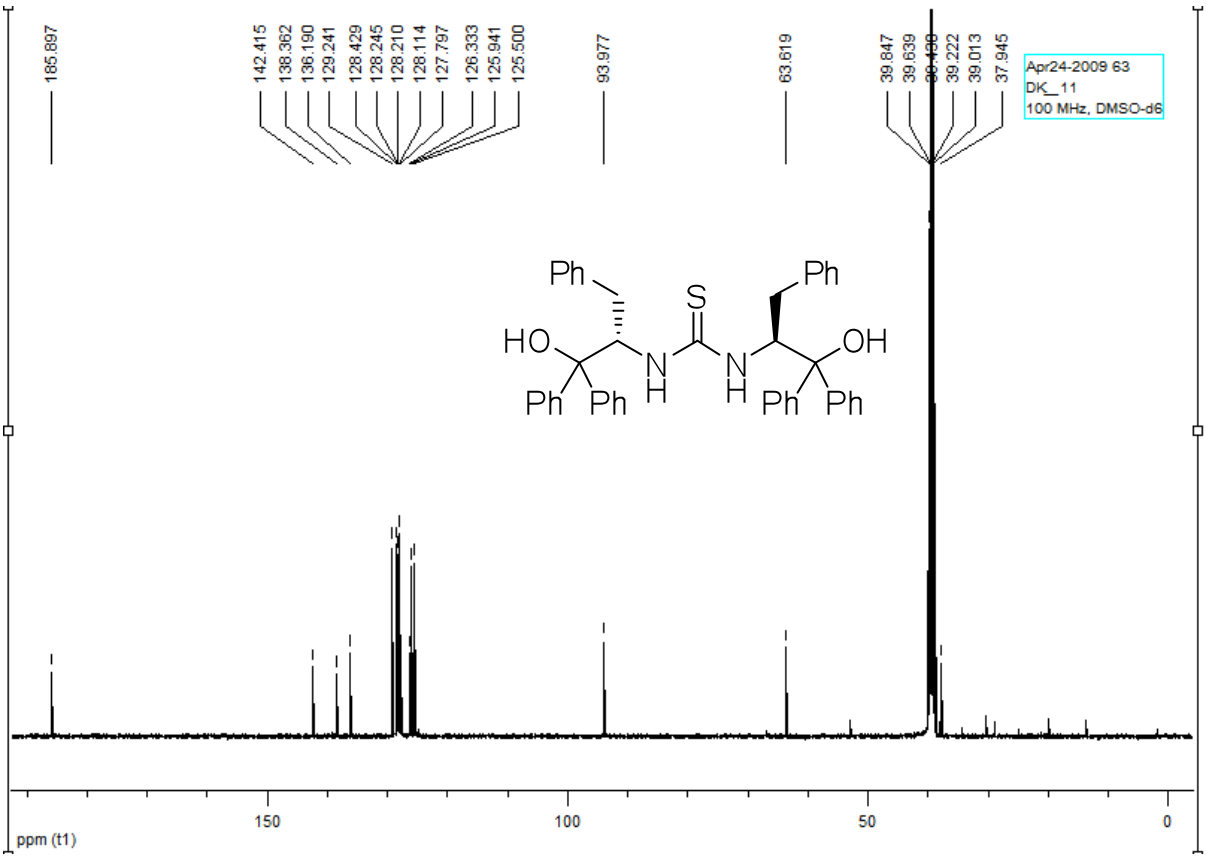
1d


8.133
7.529
7.521
7.495
7.490
7.363
7.342
7.333
7.325
7.309
7.304
7.298
7.260
4.499
4.483
1.913
1.896
1.886
1.869
1.859
1.851
1.841
1.730
1.720
0.928
0.900
0.703
0.676
Ap240S.109
DK_10
250 MHz, CDCl3
HO
Ph
Ph
N
H
S
N
H
OH
Ph
Ph
1.96
4.25
16.34
2.00
3.62
6.07
6.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

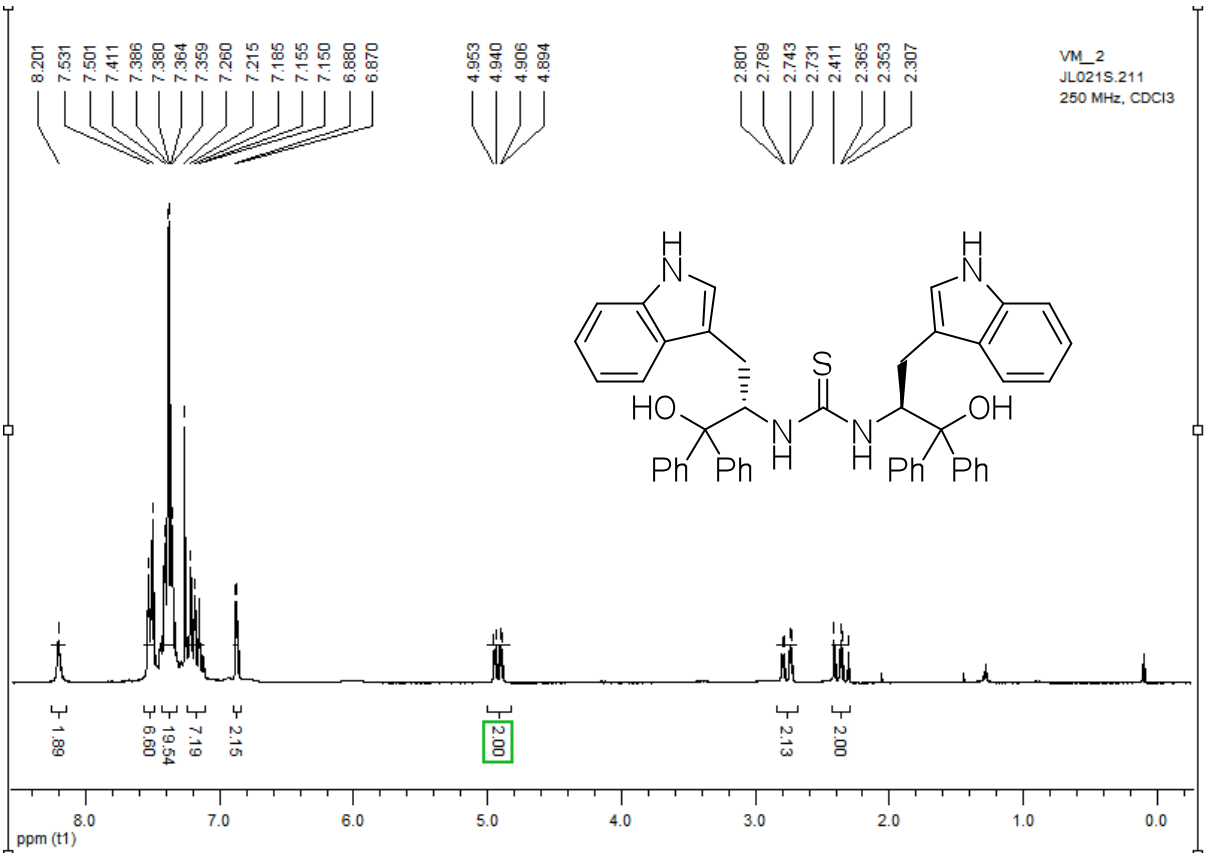

187.912
142.388
138.010
128.656
128.604
128.324
128.168
128.111
126.560
125.744
95.731
69.489
29.663
20.867
16.281
Sep17 2009 91
DK_10
100 MHz, CDCl3
HO
Ph
Ph
N
H
S
N
H
OH
Ph
Ph
150
100
50
0
ppm (t1)

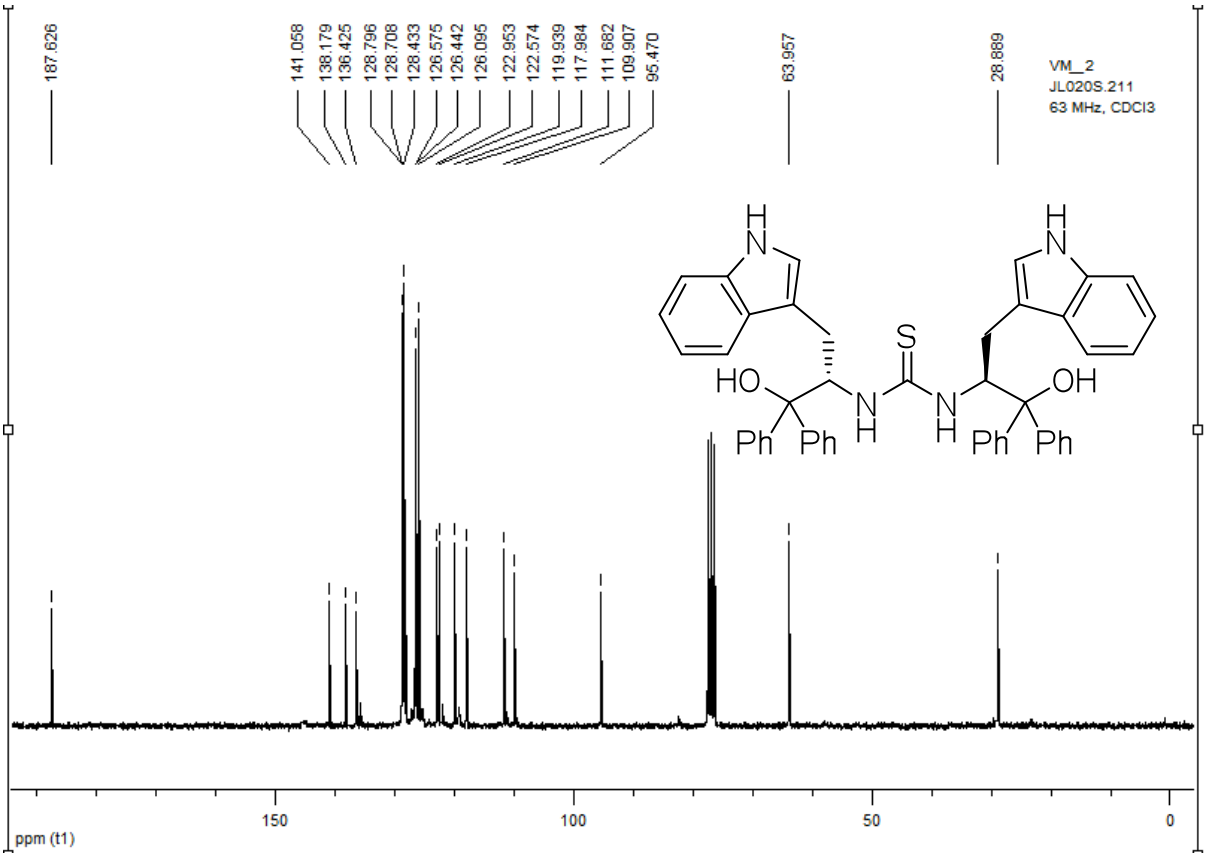
1e


10.317
7.650
7.632
7.416
7.397
7.383
7.372
7.364
7.346
7.244
7.226
7.122
7.118
7.102
5.064
5.053
5.041
5.029
3.343
2.610
2.599
2.576
2.565
2.509
2.505
2.500
2.495
2.491
2.332
2.308
2.297
2.273
Apr24-2009 60
DK_11
400 MHz, DMSO-d6
Ph
HO
Ph
Ph
N
H
S
N
H
Ph
OH
Ph
Ph
1.93
4.04
1.65
0.40
0.06
2.00
1.04
2.00
2.59
10.0
5.0
0.0
ppm (t1)

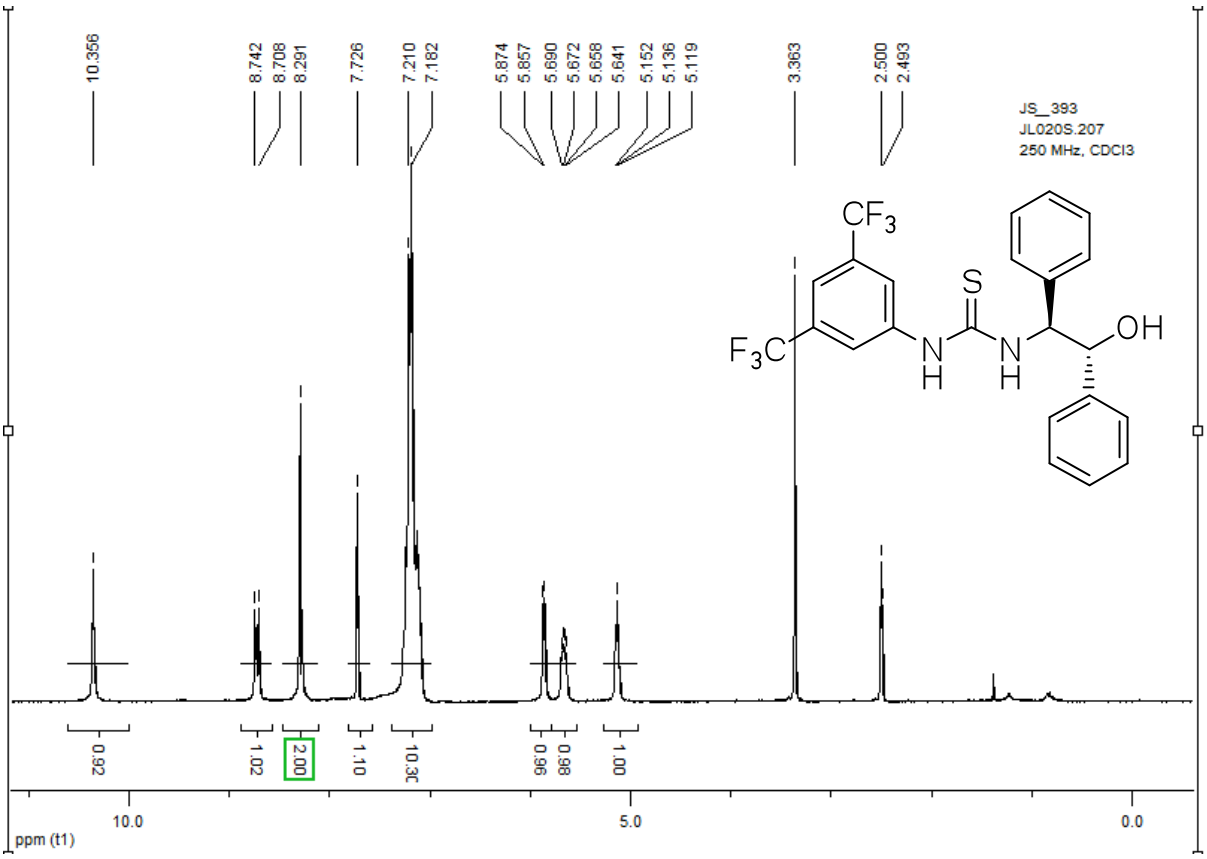

185.897
142.415
138.362
136.190
129.241
128.429
128.245
128.210
128.114
127.797
126.333
125.941
125.500
93.977
63.619
39.847
39.639
39.430
39.222
39.013
37.945
Apr24-2009 63
DK_11
100 MHz, DMSO-d6
Ph
HO
Ph
Ph
N
H
S
N
H
Ph
OH
Ph
Ph
150
100
50
0
ppm (t1)

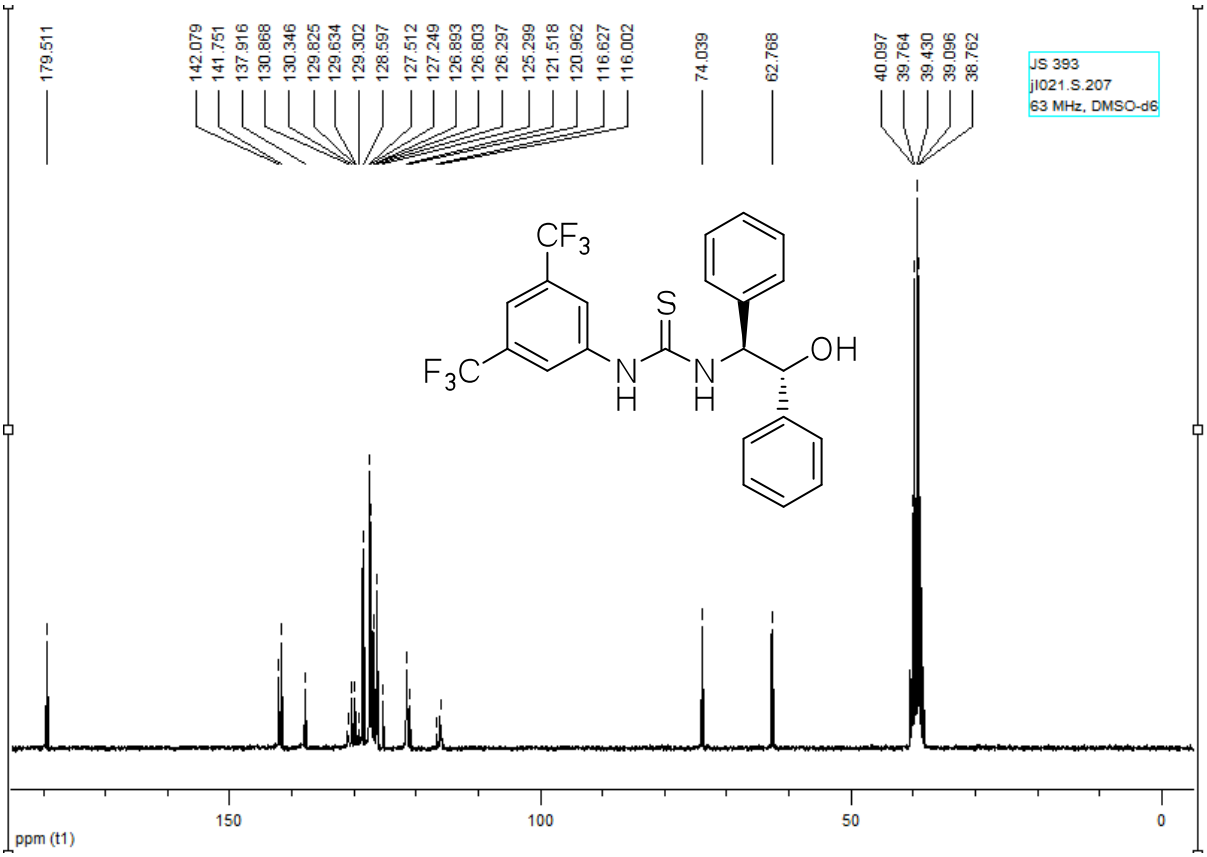
1f

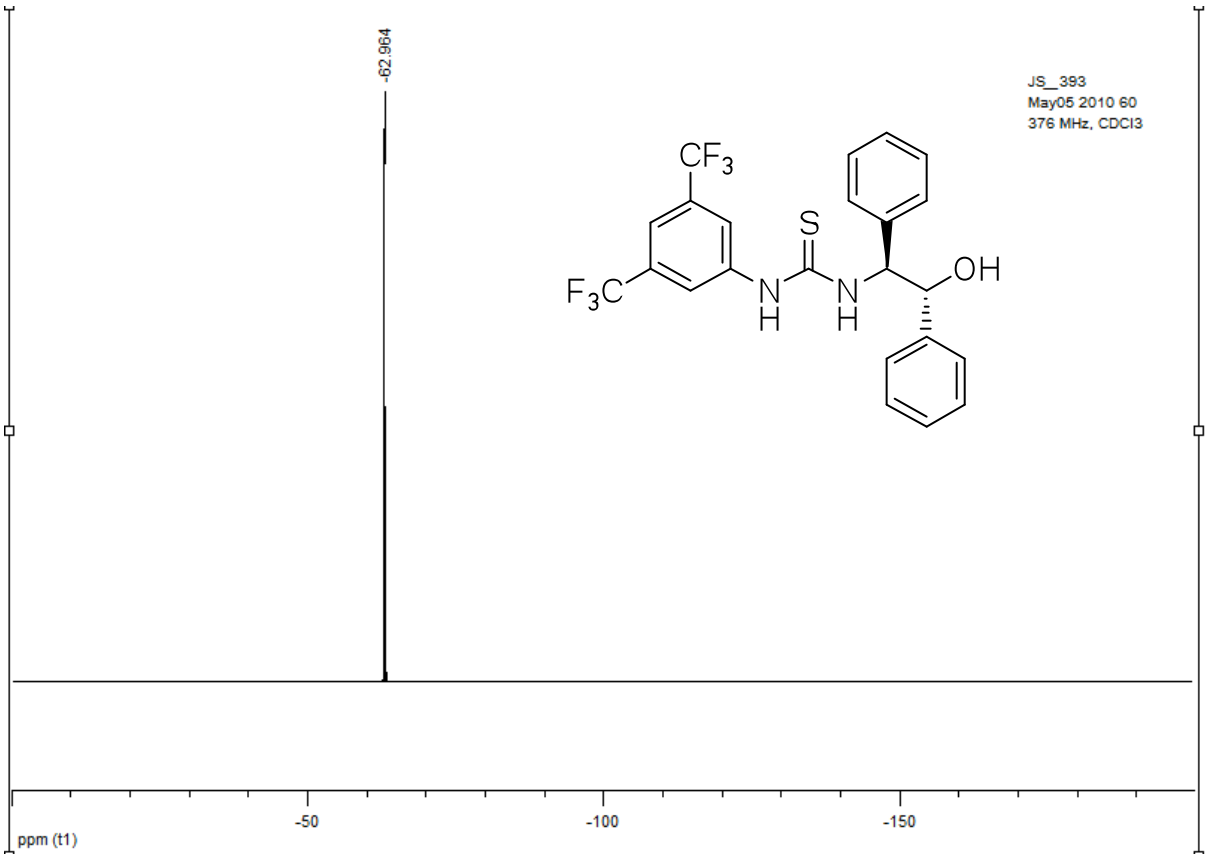

8.201
7.531
7.501
7.411
7.386
7.380
7.364
7.359
7.260
7.215
7.185
7.155
7.150
6.880
6.870
4.953
4.940
4.906
4.894
2.801
2.789
2.743
2.731
2.411
2.365
2.353
2.307
VM_2
JL021S.211
250 MHz, CDCl3
1.89
6.60
19.54
7.19
2.15
2.00
2.13
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


187.626
141.058
138.179
136.425
128.796
128.708
128.433
126.575
126.442
126.095
122.953
122.574
119.939
117.984
111.682
109.907
95.470
63.957
28.889
VM_2
JL020S.211
63 MHz, CDCl3
150
100
50
0
ppm (t1)

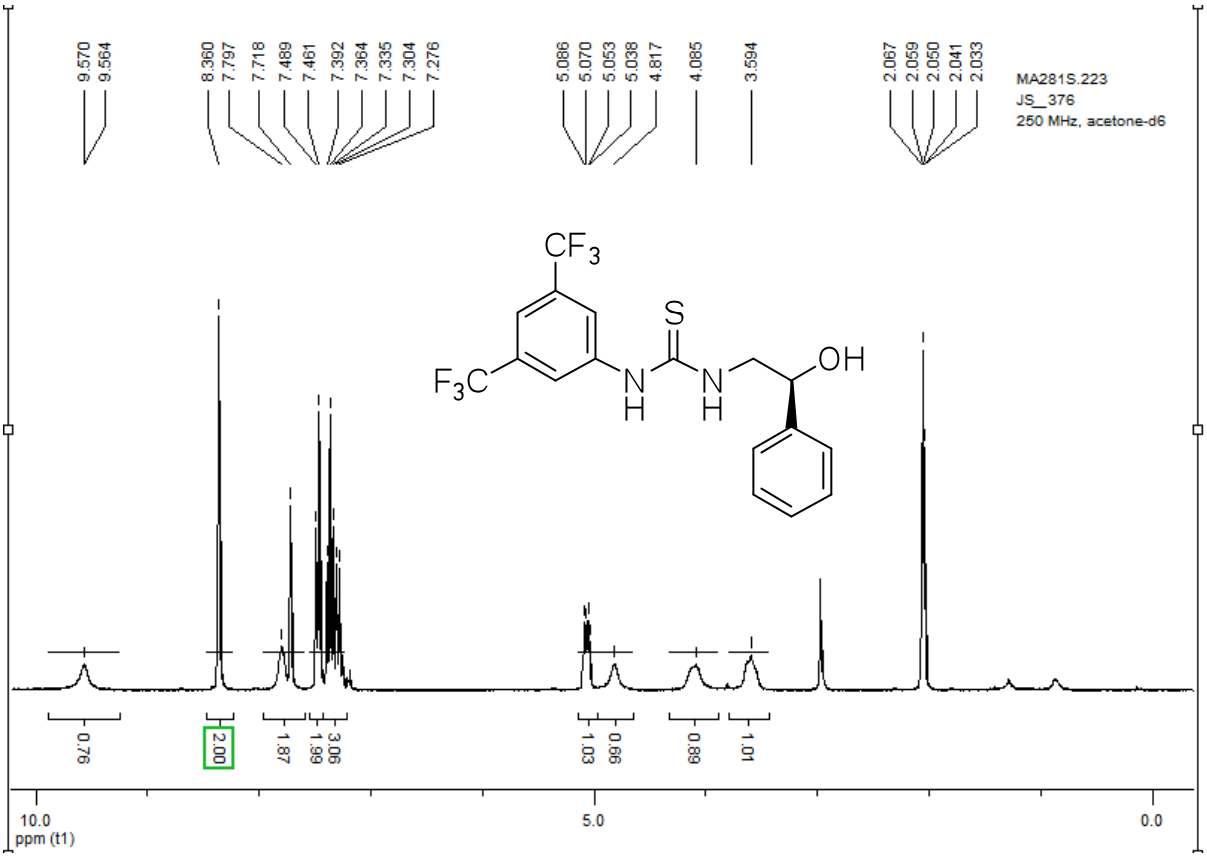
1g

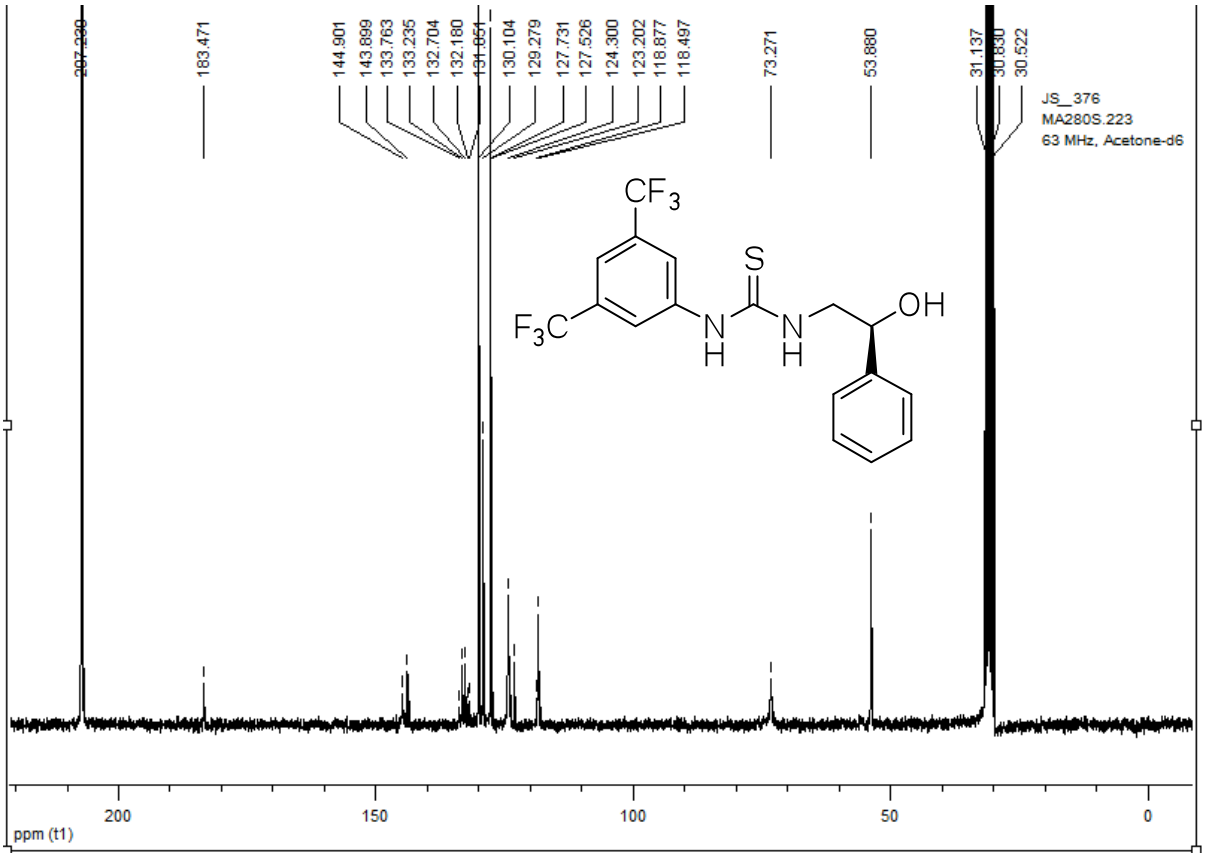


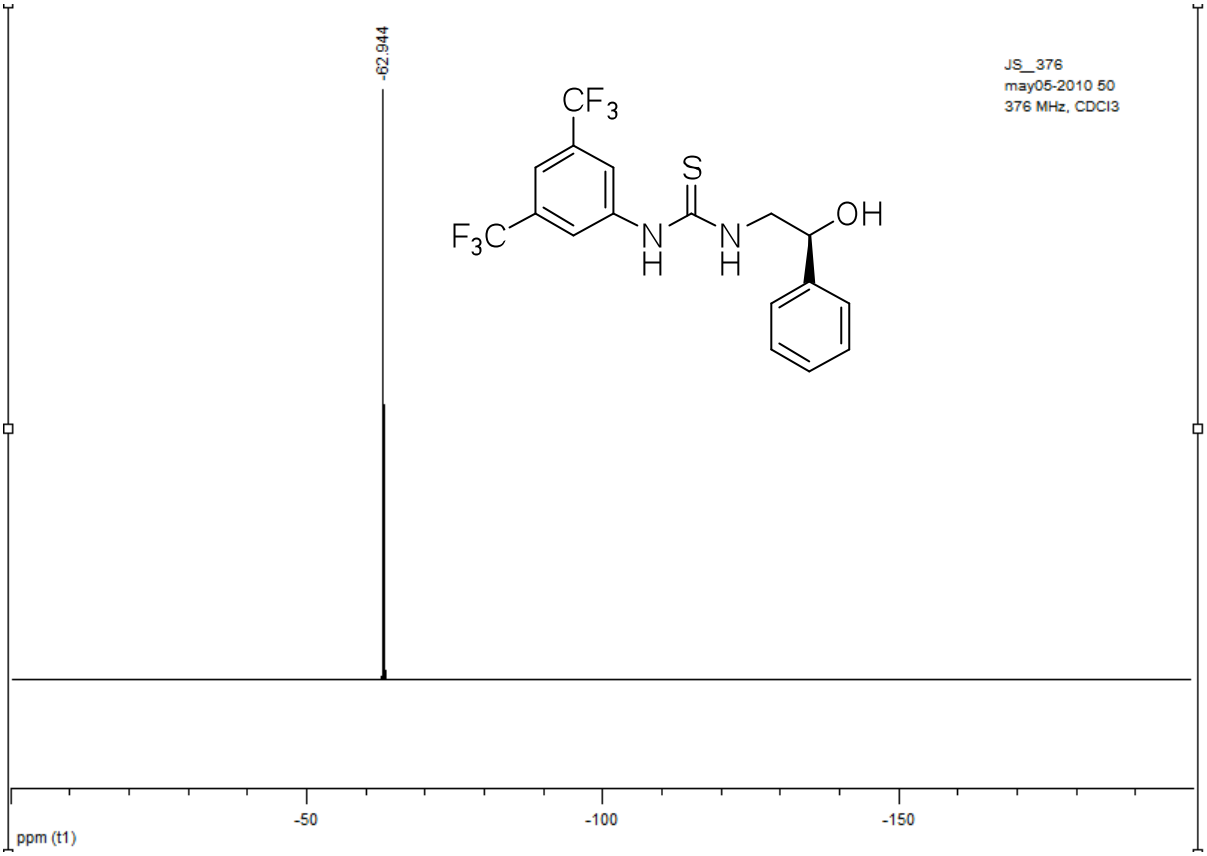



-62.964
JS_393
May05 2010 60
376 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
-50
-100
-150
ppm (t1)

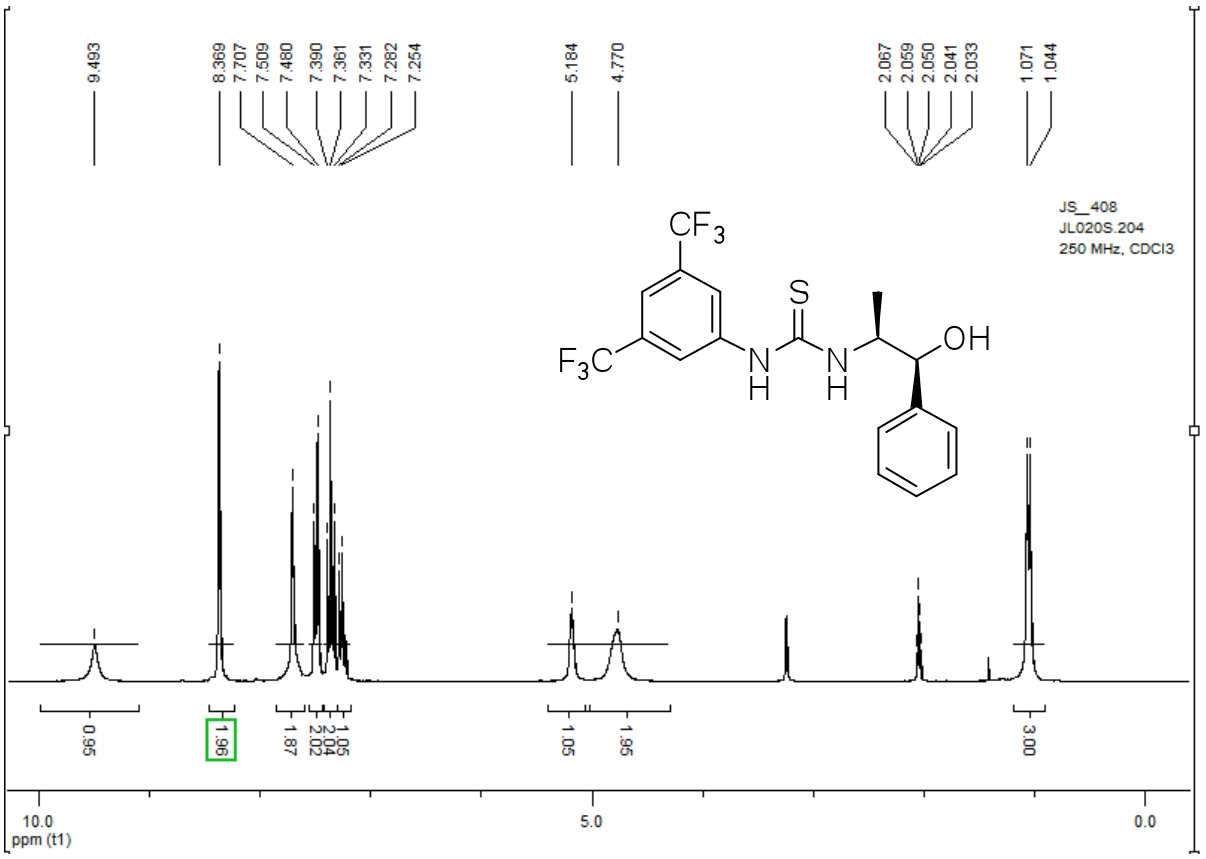
1h

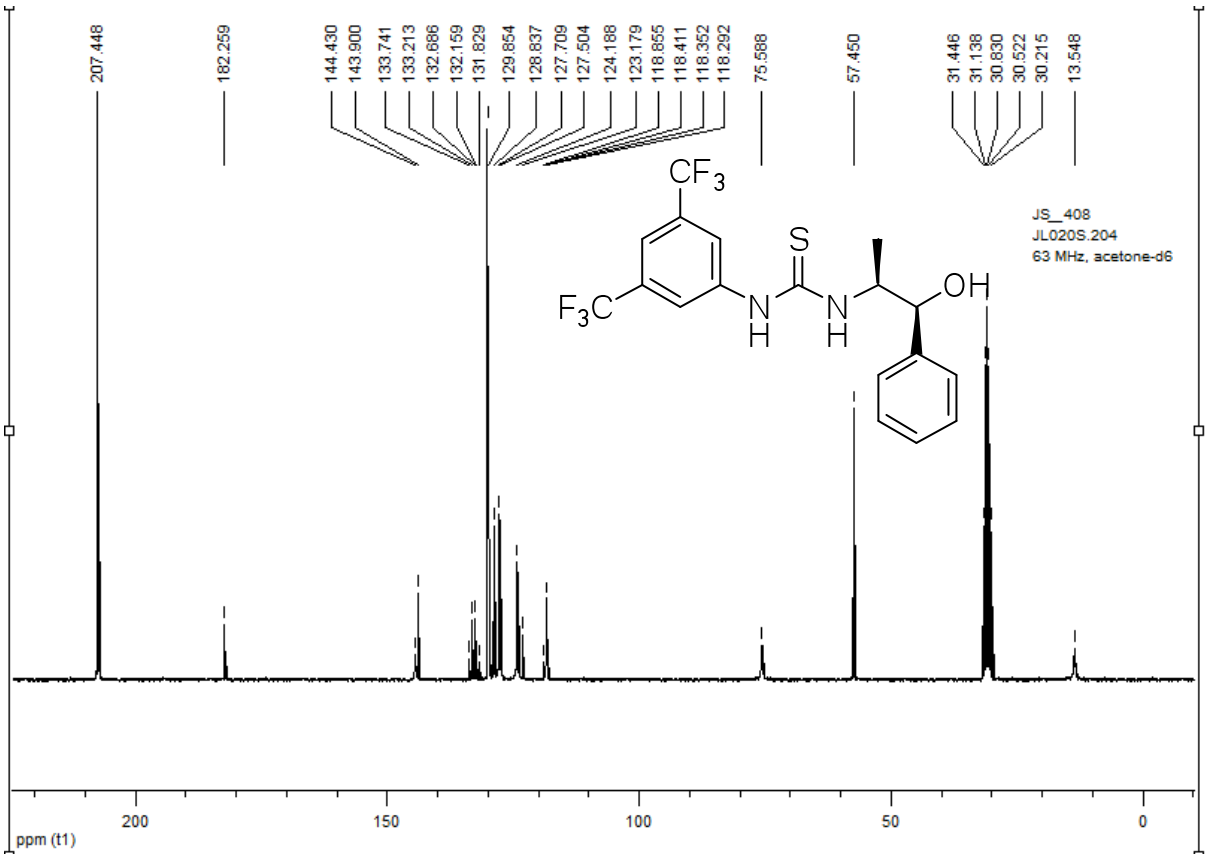

9.570
9.564
8.360
7.797
7.718
7.489
7.461
7.392
7.364
7.335
7.304
7.276
5.086
5.070
5.053
5.038
4.817
4.085
3.594
2.067
2.059
2.050
2.041
2.033
MA281S.223
JS_376
250 MHz, acetone-d6
CF3
F3C
S
N
H
N
H
OH
0.76
2.00
1.87
3.06
1.99
1.03
0.66
0.89
1.01
10.0
ppm (t1)
5.0
0.0

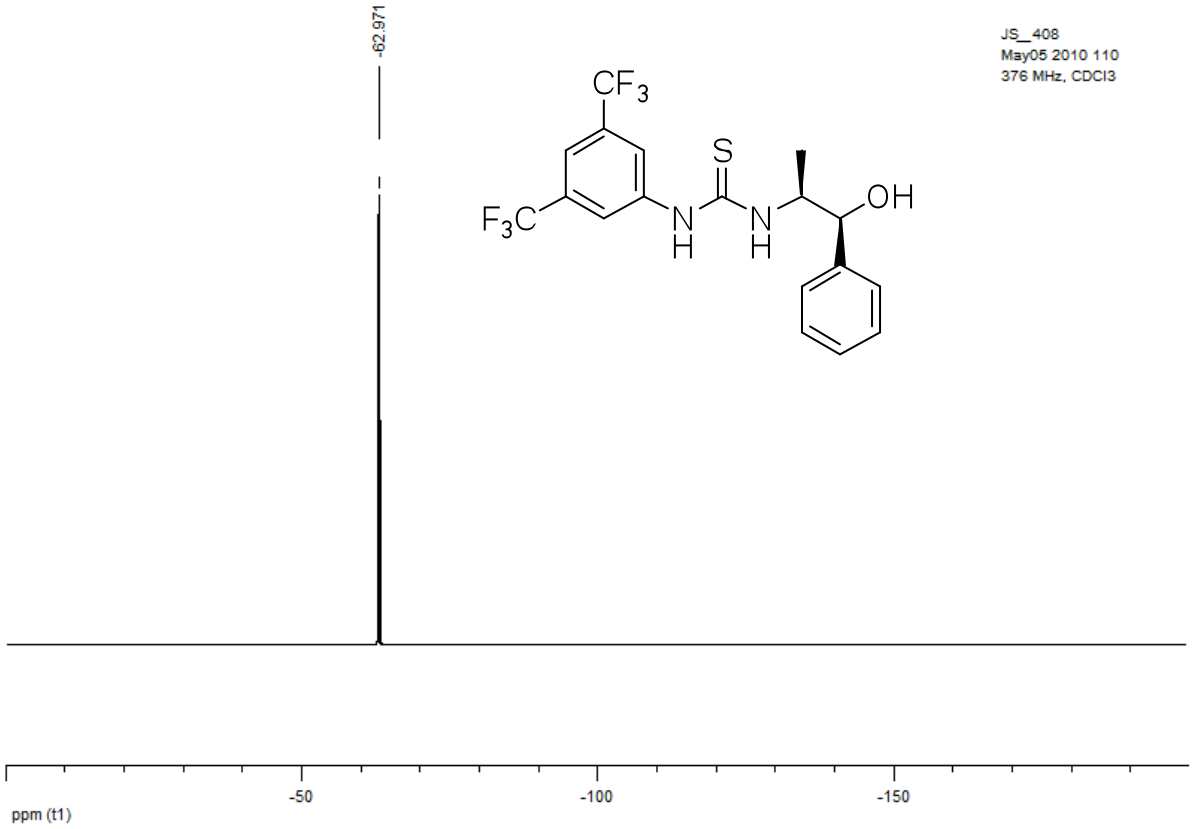

207.230
183.471
144.901
143.899
133.763
133.235
132.704
132.180
131.851
130.104
129.279
127.731
127.526
124.300
123.202
118.877
118.497
73.271
53.880
31.137
30.830
30.522
JS_376
MA280S.223
63 MHz, Acetone-d6
CF3
F3C
S
N
H
N
H
OH
200
150
100
50
0
ppm (t1)



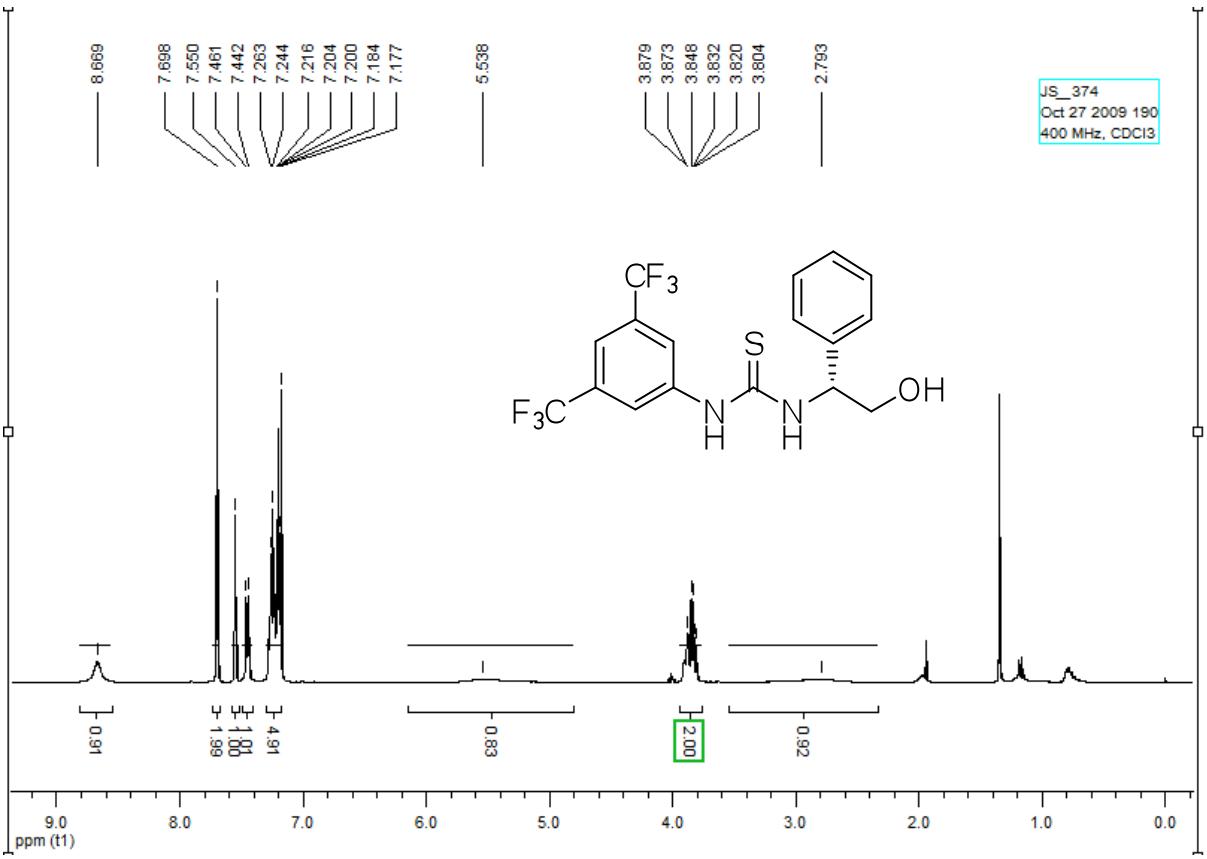
1i

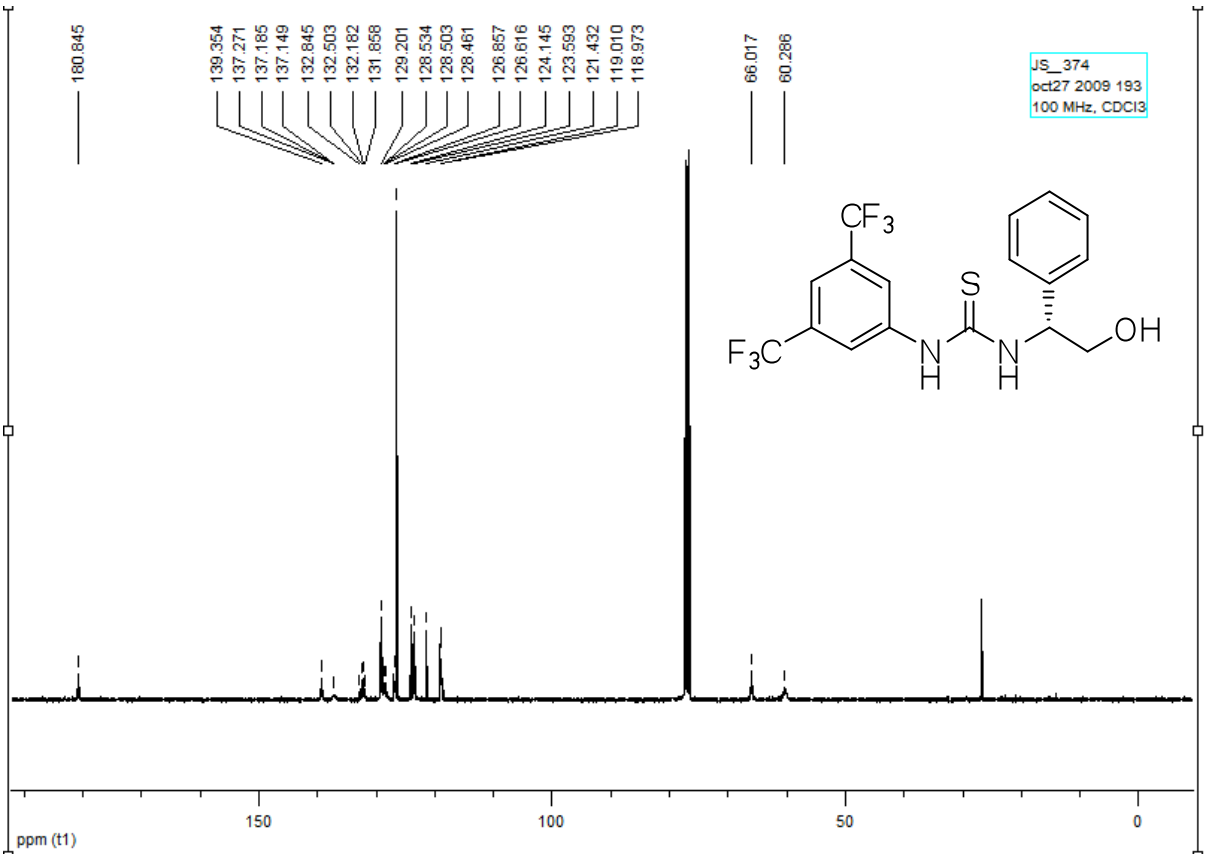

9.493
8.369
7.707
7.509
7.480
7.390
7.361
7.331
7.282
7.254
5.184
4.770
2.067
2.059
2.050
2.041
2.033
1.071
1.044
JS_408
JL020S.204
250 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
0.96
1.96
1.87
2.02
2.04
1.05
1.05
1.95
3.00
10.0
ppm (t1)
5.0
0.0

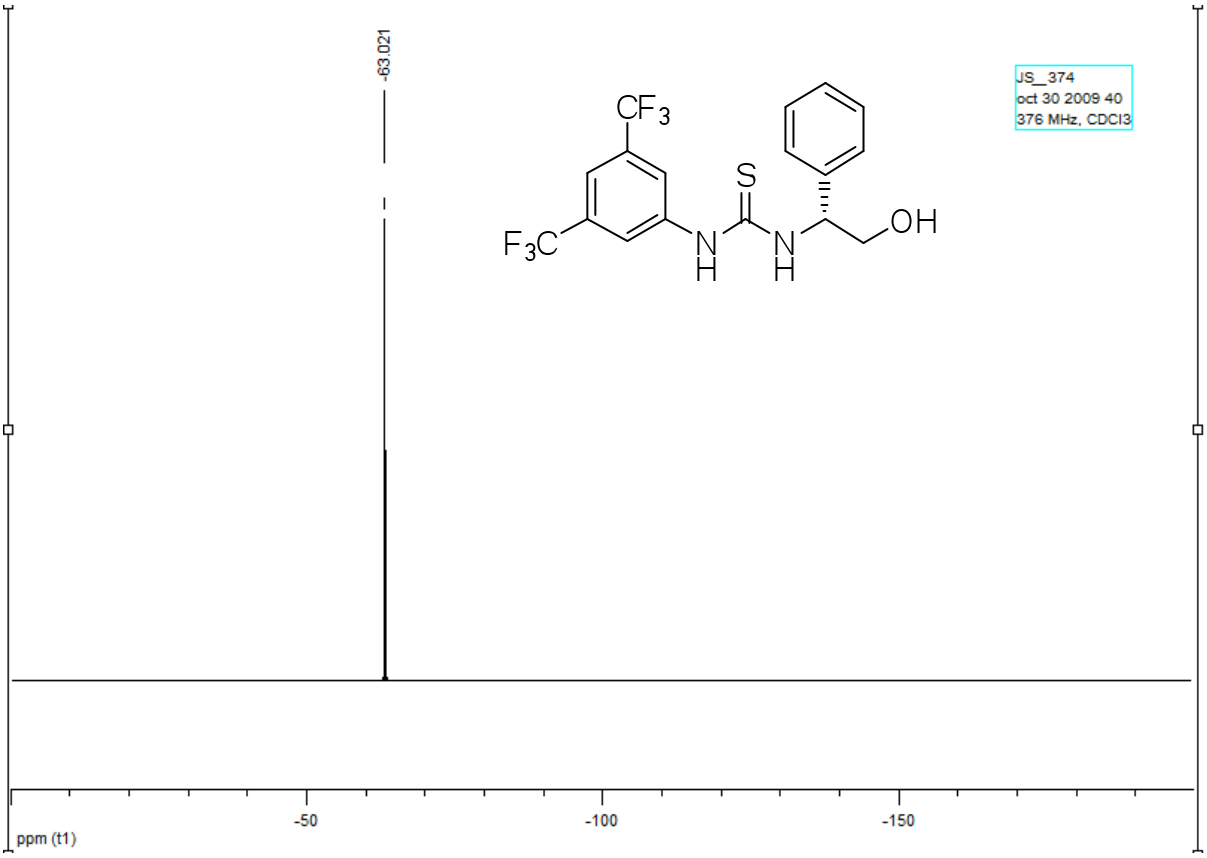

207.448
182.259
144.430
143.900
133.741
133.213
132.686
132.159
131.829
129.854
128.837
127.709
127.504
124.188
123.179
118.855
118.411
118.352
118.292
75.588
57.450
31.446
31.138
30.830
30.522
30.215
13.548
JS_408
JL020S.204
63 MHz, acetone-d6
CF3
F3C
S
N
H
N
H
OH
200
150
100
50
0
ppm (t1)



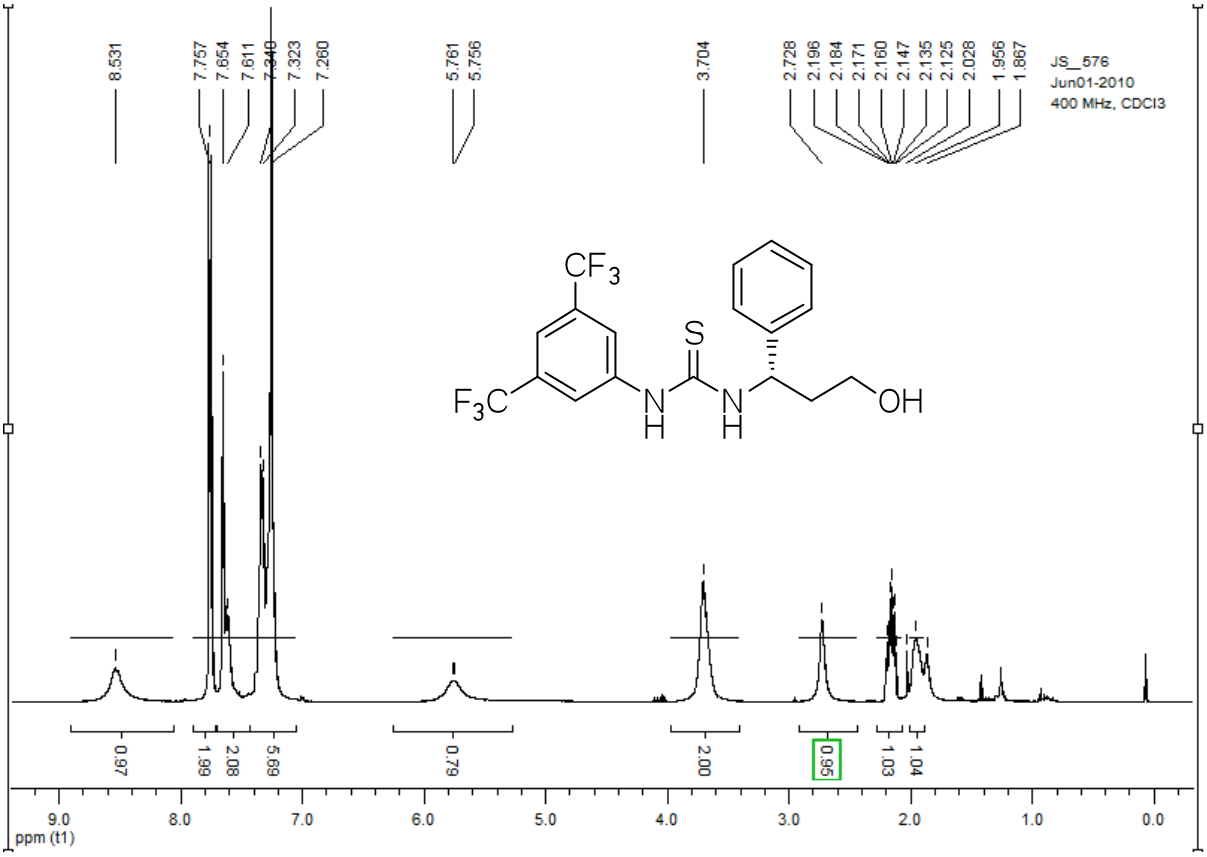
1j

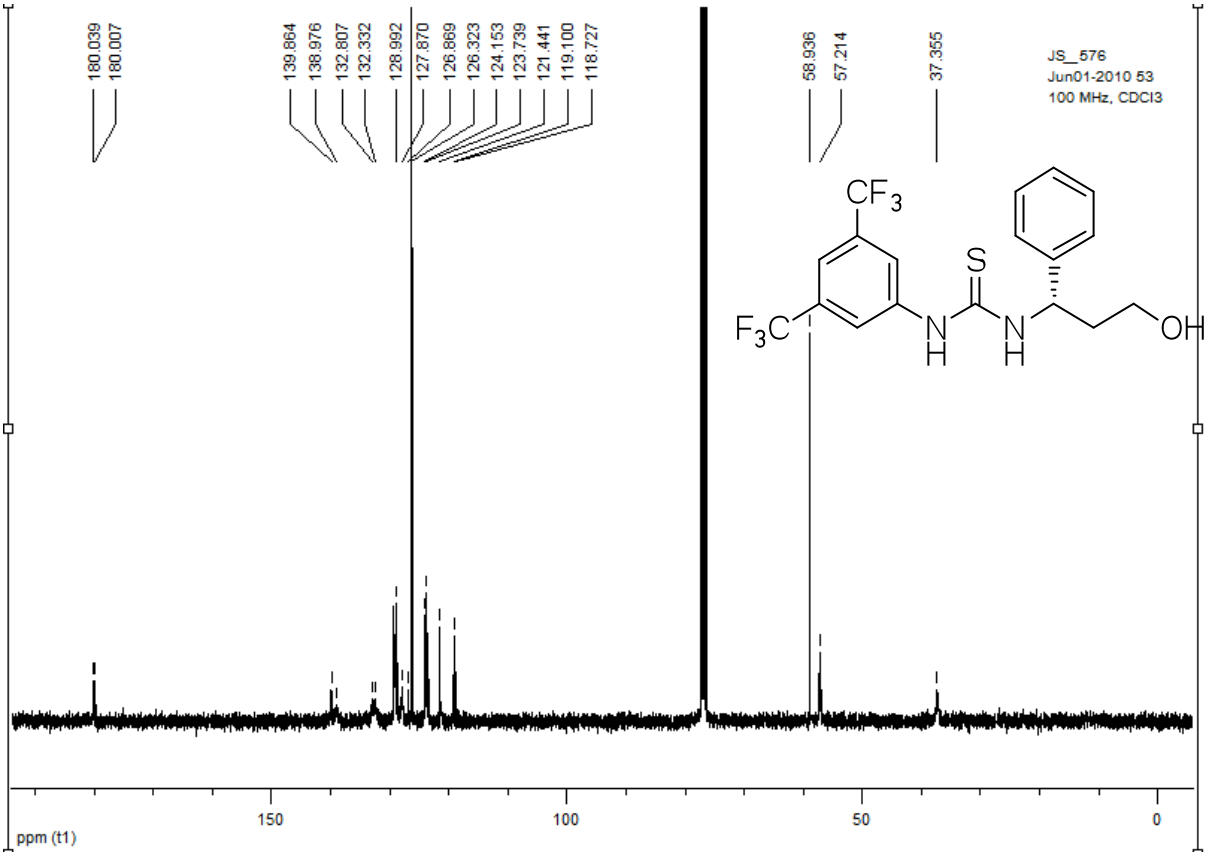

8.669
7.698
7.550
7.461
7.442
7.263
7.244
7.216
7.204
7.200
7.184
7.177
5.538
3.879
3.873
3.848
3.832
3.820
3.804
2.793
JS_374
Oct 27 2009 190
400 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
0.91
1.99
1.00
1.11
4.91
0.83
2.00
0.92
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

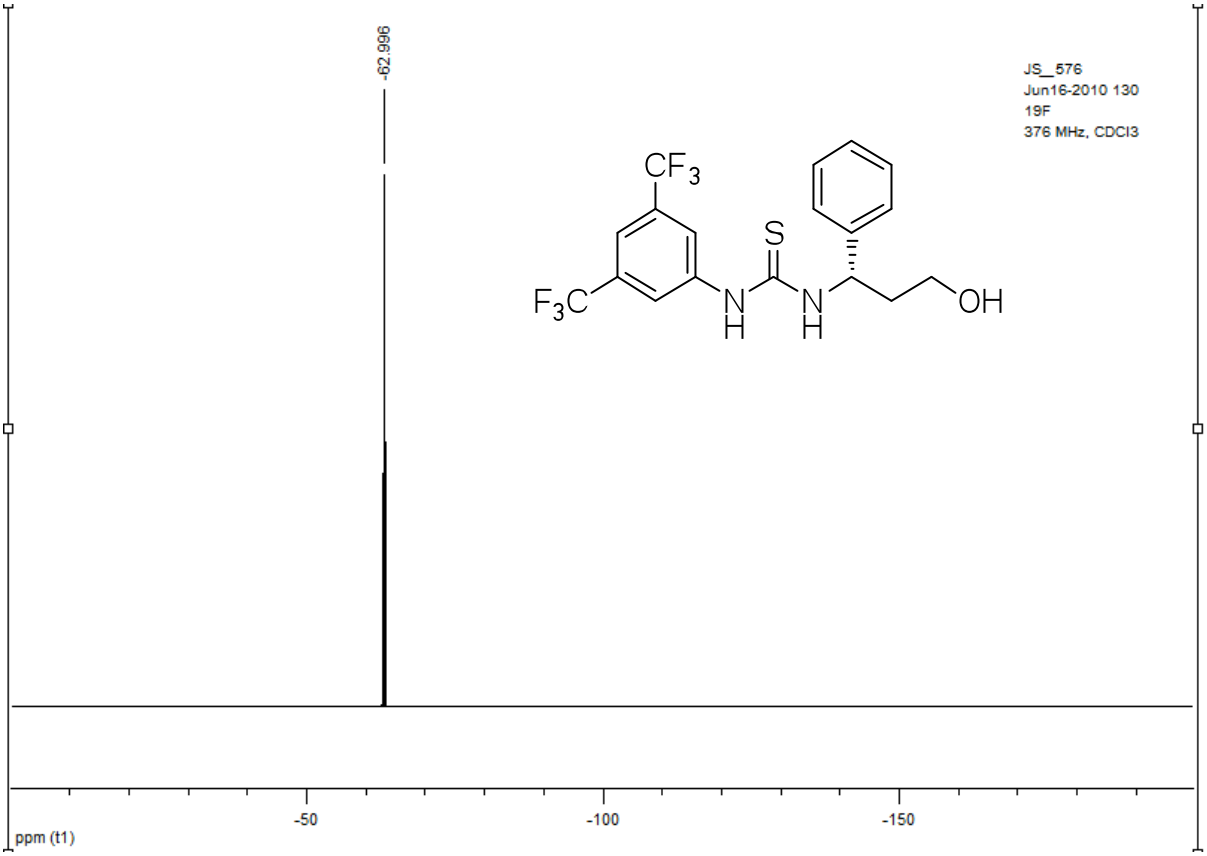

180.845
139.354
137.271
137.185
137.149
132.845
132.503
132.182
131.858
129.201
128.534
128.503
128.461
126.857
126.616
124.145
123.593
121.432
119.010
118.973
66.017
60.286
JS_374
oct27 2009 193
100 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
150
100
50
0
ppm (t1)


-63.021
JS_374
oct 30 2009 40
376 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
-50
-100
-150
ppm (t1)

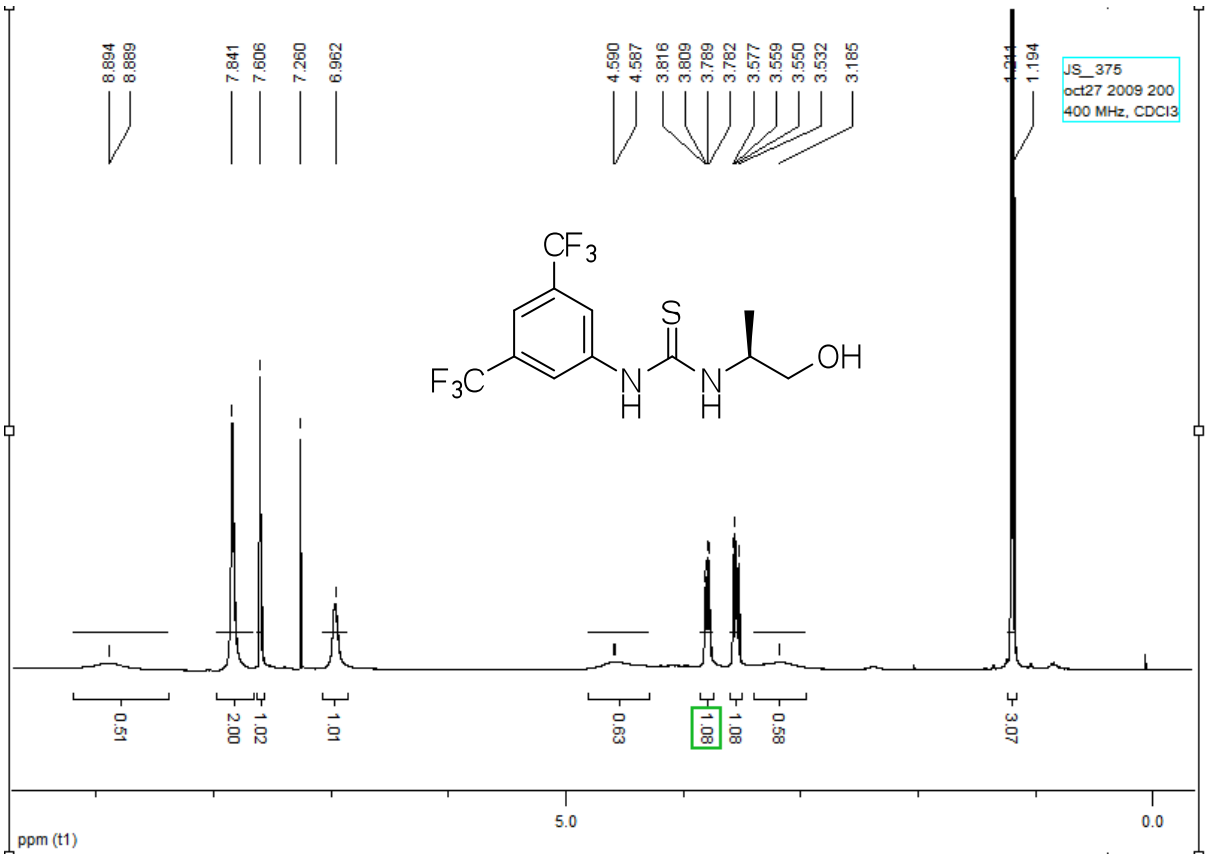
1k

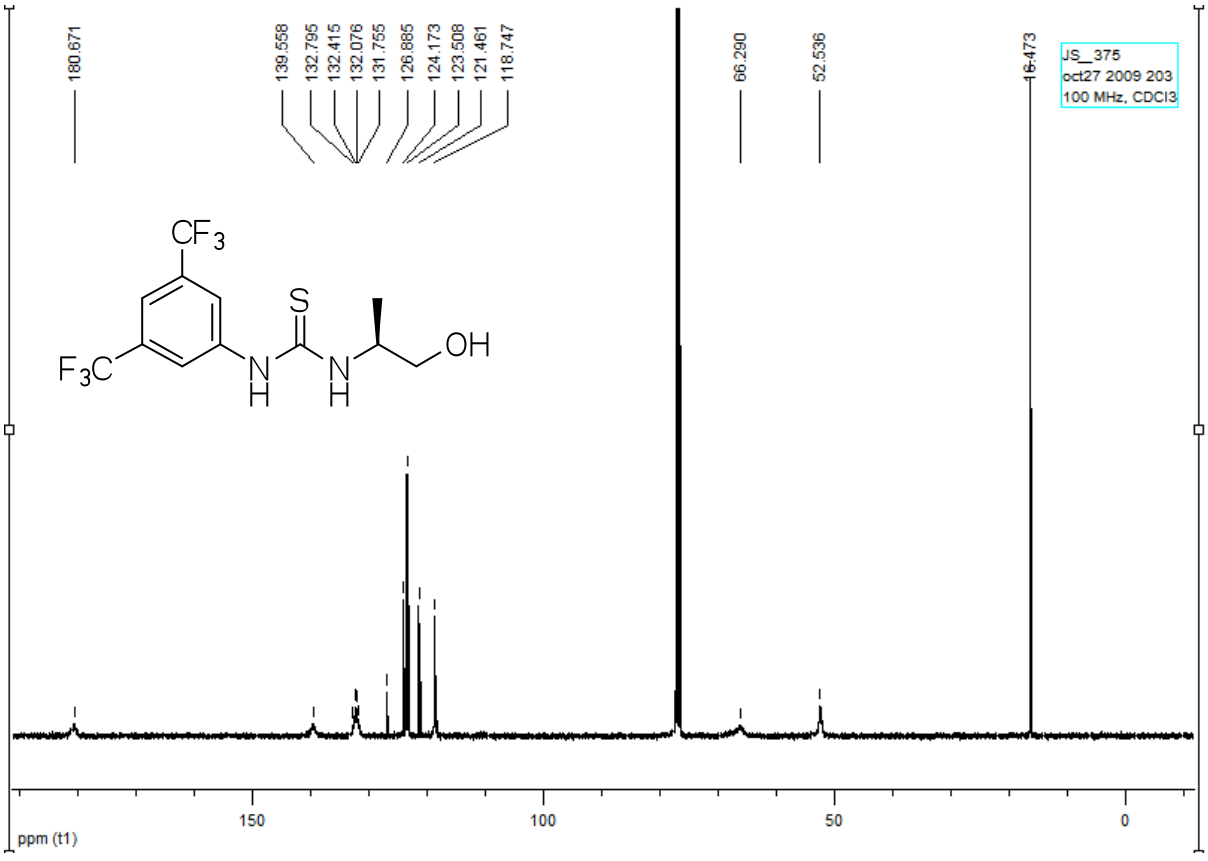

8.531
7.757
7.654
7.611
7.348
7.323
7.260
5.761
5.756
3.704
2.728
2.196
2.184
2.171
2.160
2.147
2.135
2.125
2.028
1.956
1.867
JS_576
Jun01-2010
400 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
0.97
1.99
2.08
5.69
0.79
2.00
0.95
1.03
1.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

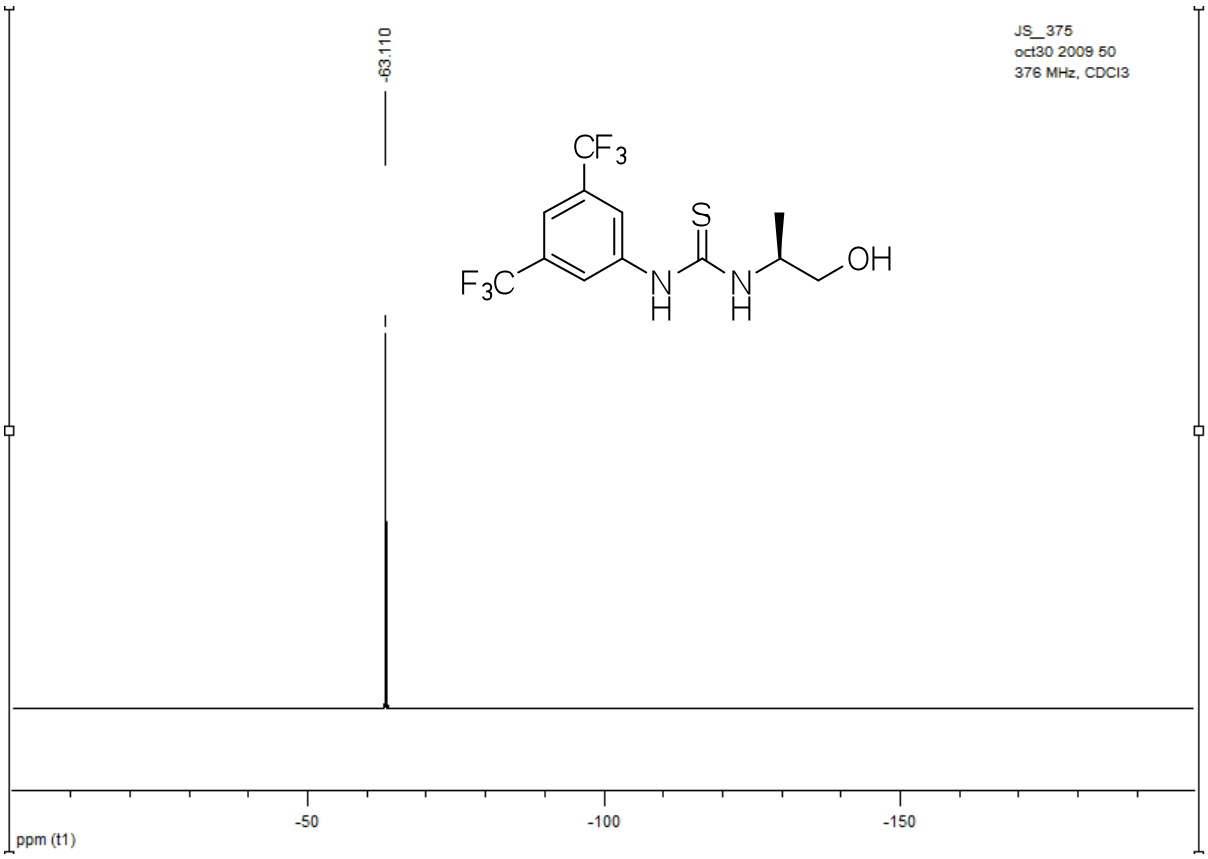

180.039
180.007
139.864
136.976
132.807
132.332
128.992
127.870
126.869
126.323
124.153
123.739
121.441
119.100
118.727
58.936
57.214
37.355
JS_576
Jun01-2010 53
100 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
150
100
50
0
ppm (t1)



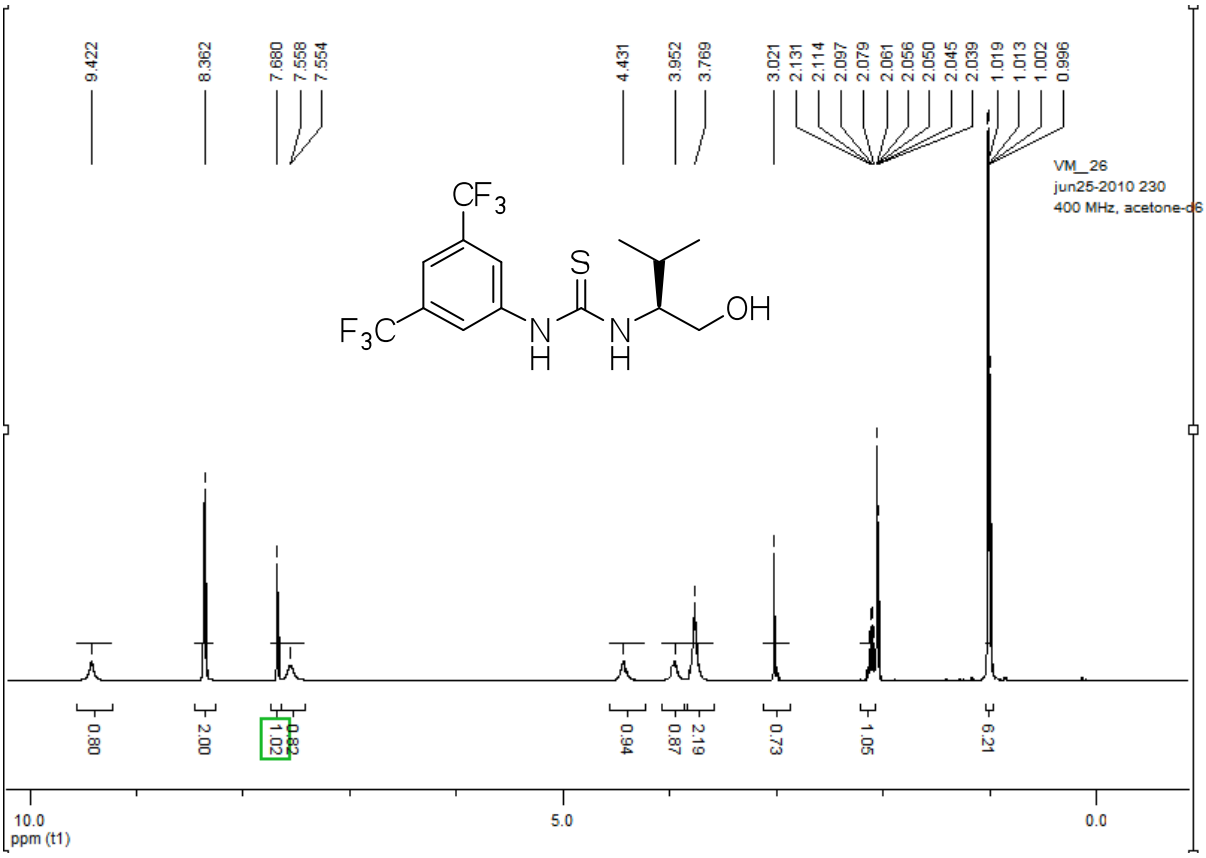
1l

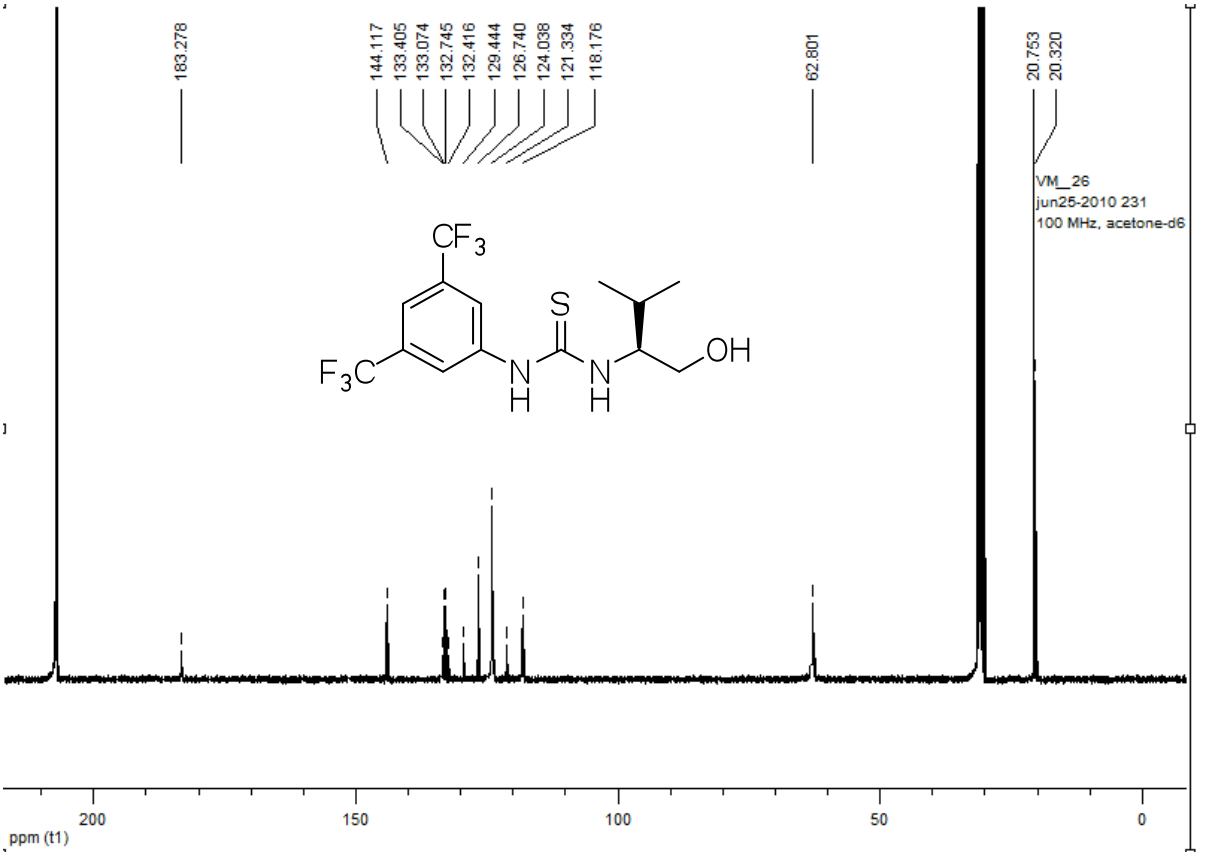

8.894
8.889
7.841
7.606
7.260
6.962
4.590
4.587
3.816
3.809
3.789
3.782
3.577
3.559
3.550
3.532
3.185
1.211
1.194
JS_375
oct27 2009 200
400 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
0.51
2.00
1.02
1.01
0.63
1.08
1.08
0.58
3.07
5.0
0.0
ppm (t1)

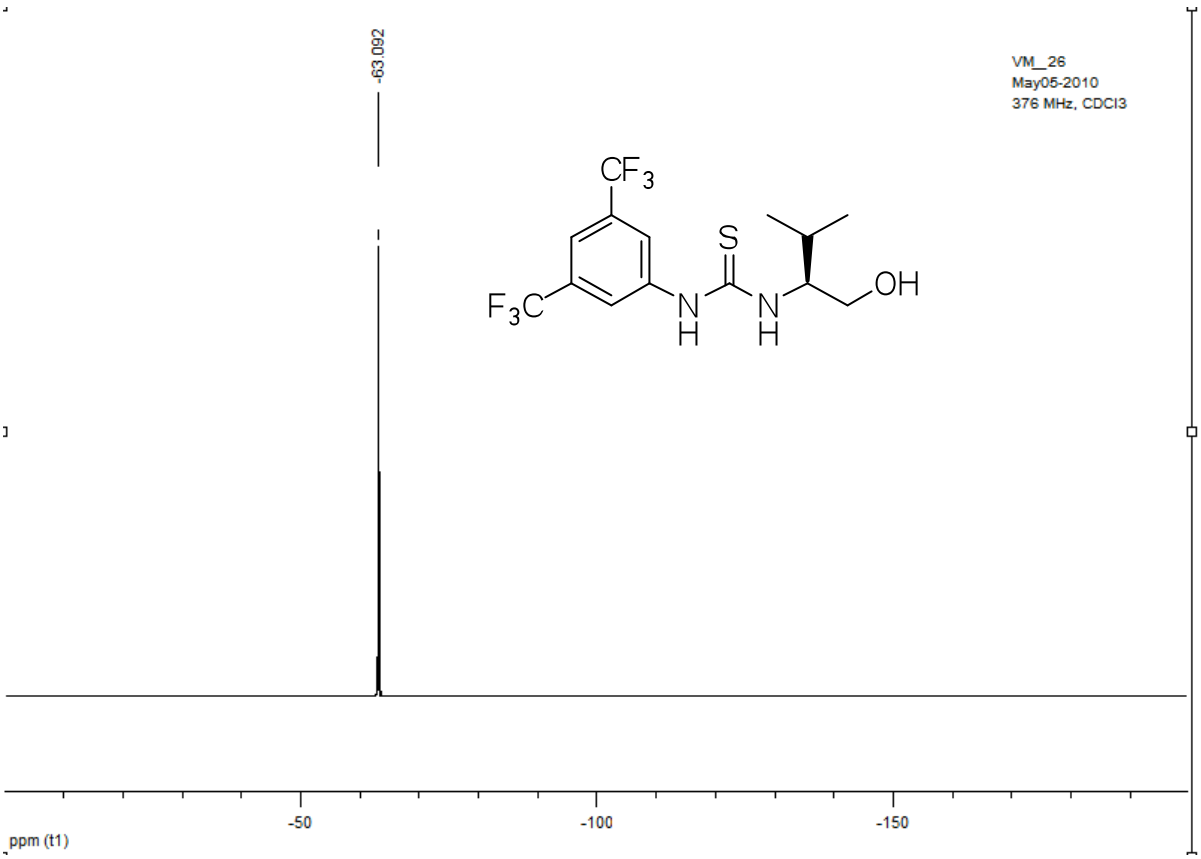

180.671
139.558
132.795
132.415
132.076
131.755
126.885
124.173
123.508
121.461
118.747
66.290
52.536
16.473
JS_375
oct27 2009 203
100 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
150
100
50
0
ppm (t1)


-63.110
JS_375
oct30 2009 50
376 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
-50
-100
-150
ppm (t1)

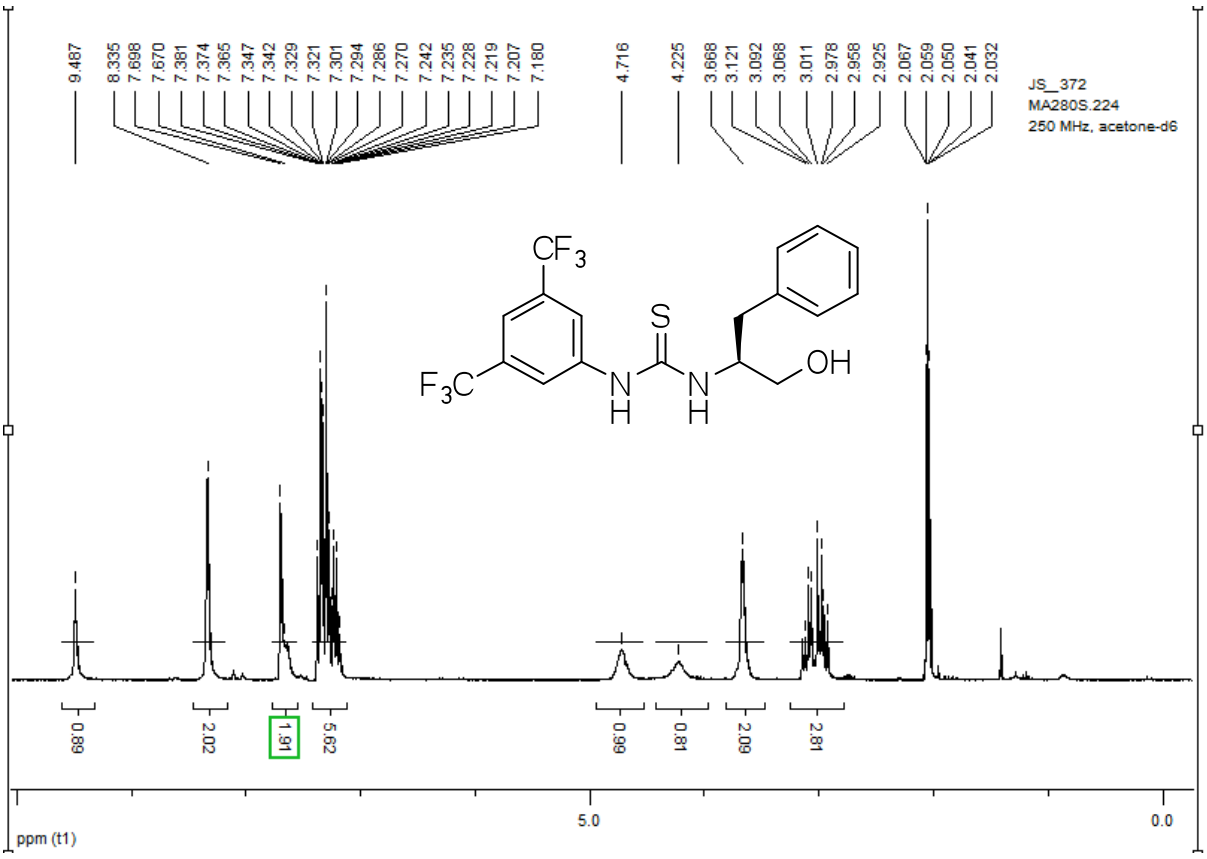
1m

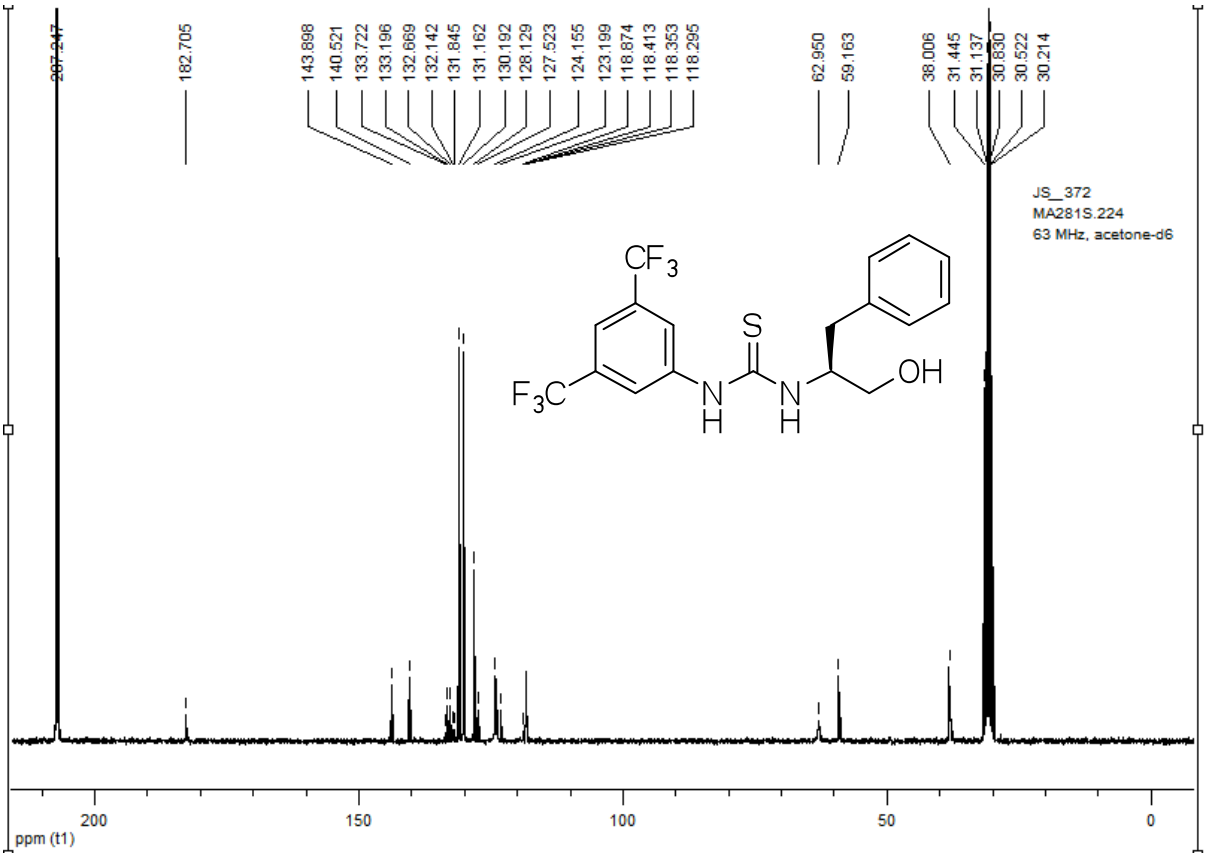

9.422
8.362
7.680
7.558
7.554
4.431
3.952
3.769
3.021
2.131
2.114
2.097
2.079
2.061
2.056
2.050
2.045
2.039
1.019
1.013
1.002
0.996
VM_26
jun25-2010 230
400 MHz, acetone-d6
CF3
F3C
S
N
H
N
H
OH
0.80
2.00
1.02
0.82
0.94
0.87
2.19
0.73
1.05
6.21
10.0
ppm (t1)
5.0
0.0

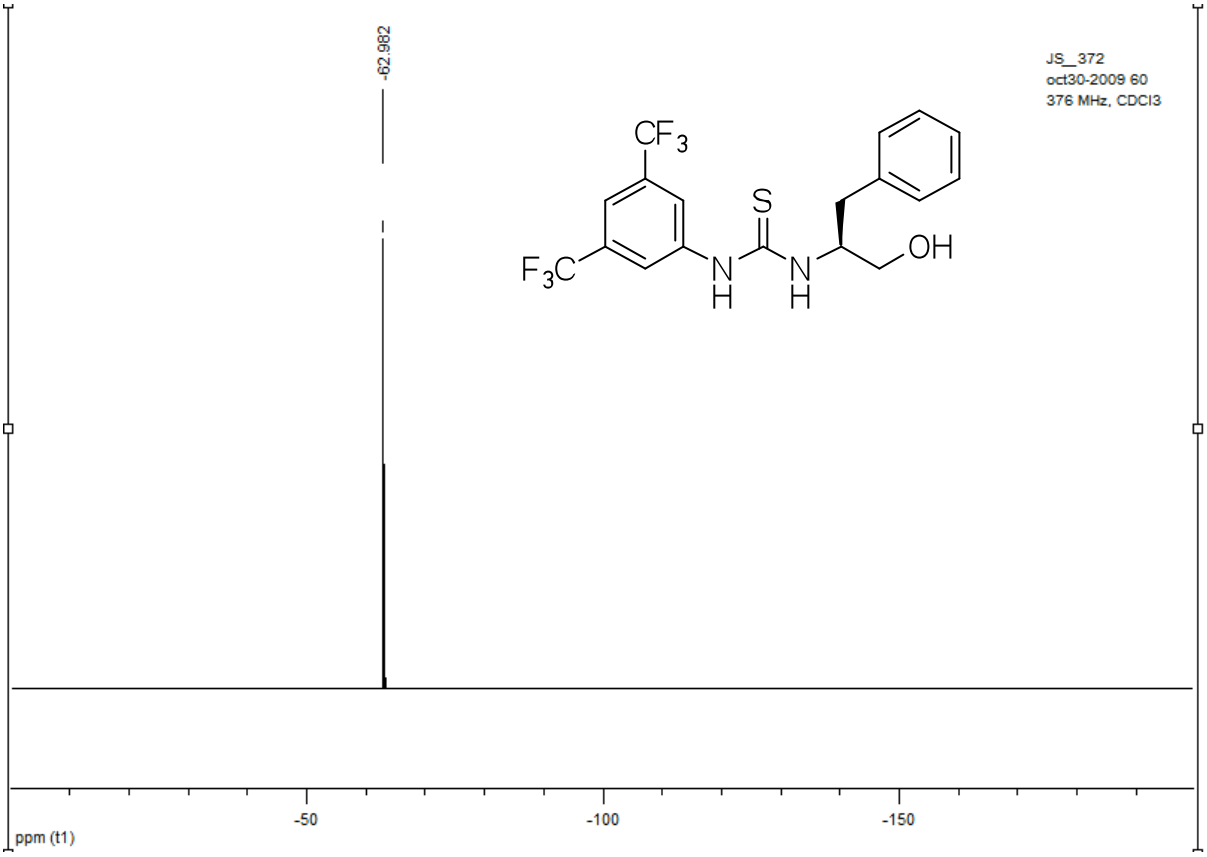

183.278
144.117
133.405
133.074
132.745
132.416
129.444
126.740
124.038
121.334
118.176
62.801
20.753
20.320
VM_26
jun25-2010 231
100 MHz, acetone-d6
CF3
F3C
S
N
H
N
H
OH
200
150
100
50
0
ppm (t1)


-63.092
VM_26
May05-2010
376 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
-50
-100
-150
ppm (t1)

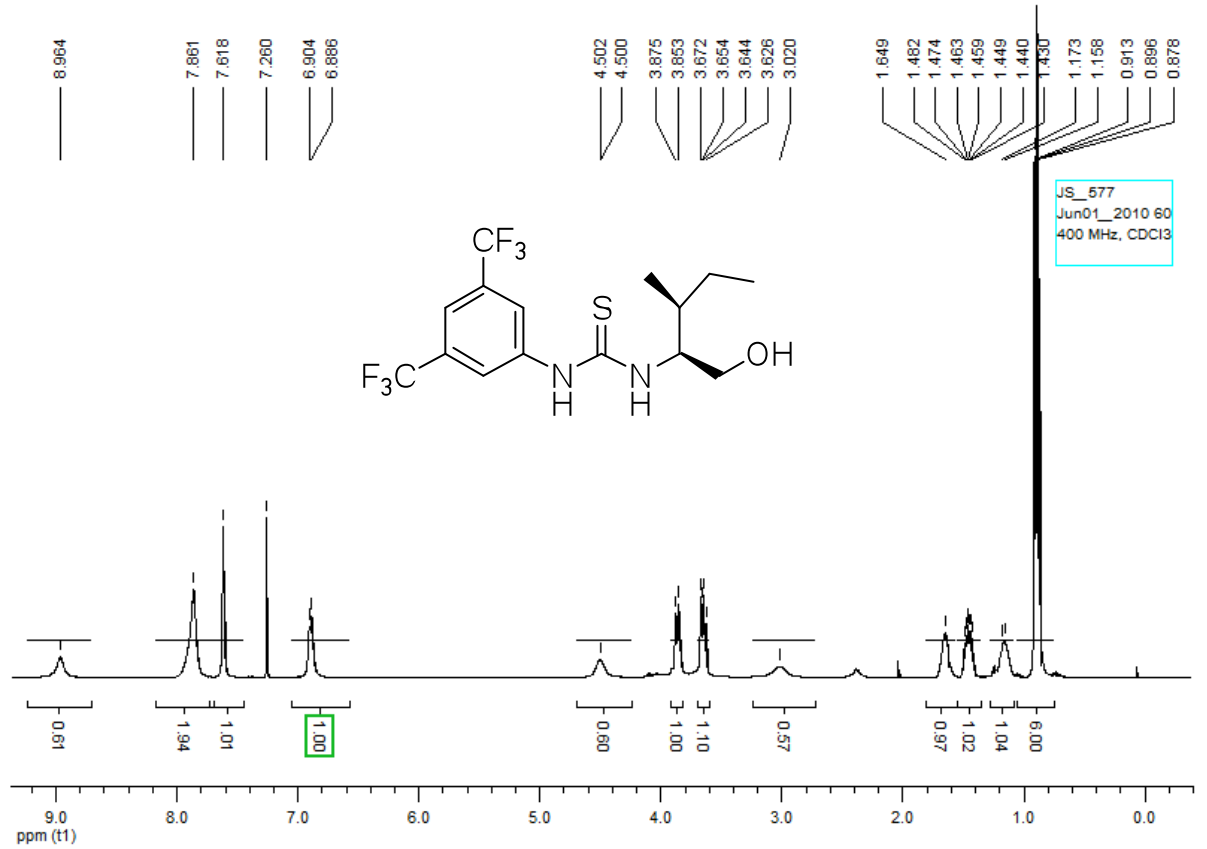
1n

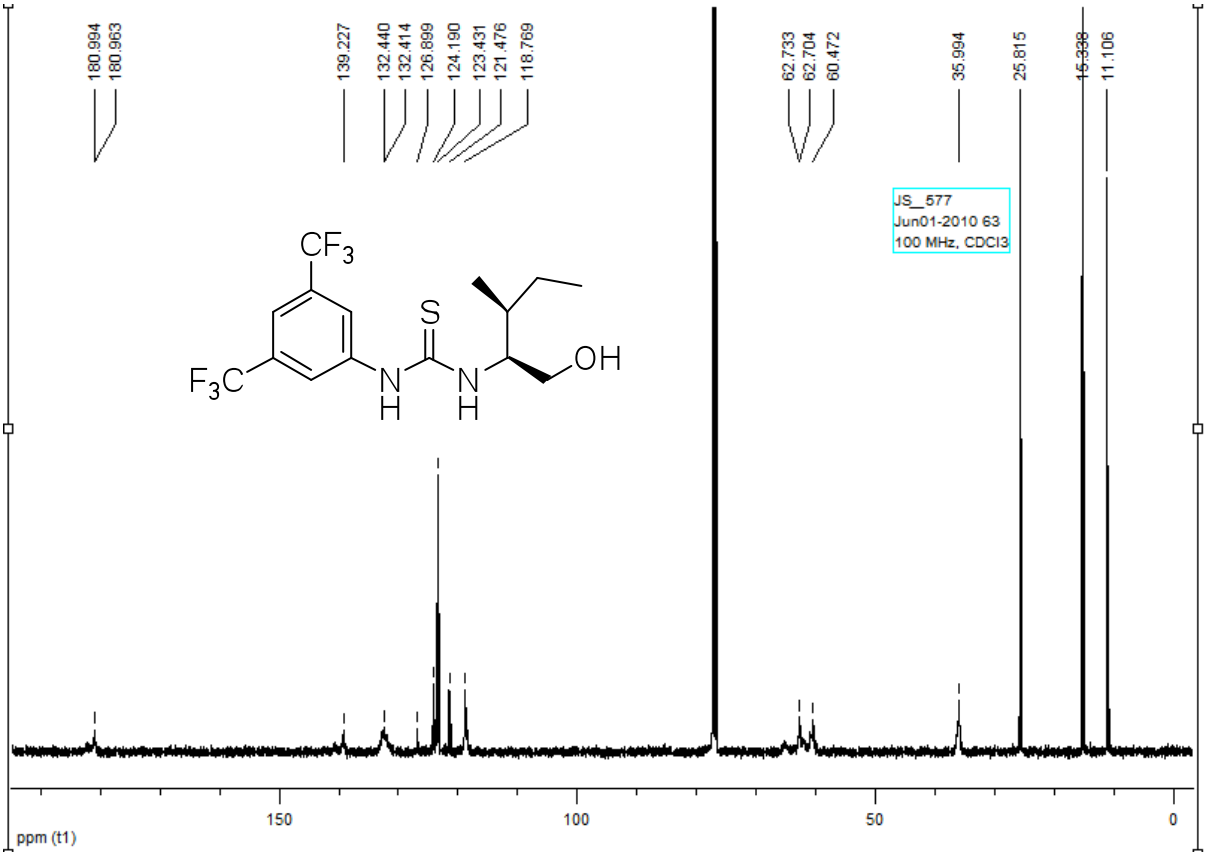

9.487
8.335
7.698
7.670
7.381
7.374
7.365
7.347
7.342
7.329
7.321
7.301
7.294
7.286
7.270
7.242
7.235
7.228
7.219
7.207
7.180
4.716
4.225
3.668
3.121
3.092
3.068
3.011
2.978
2.958
2.925
2.067
2.059
2.050
2.041
2.032
JS_372
MA280S.224
250 MHz, acetone-d6
CF3
S
F3C
N
H
N
H
OH
0.89
2.02
1.91
5.62
0.99
0.81
2.09
2.81
5.0
0.0
ppm (t1)

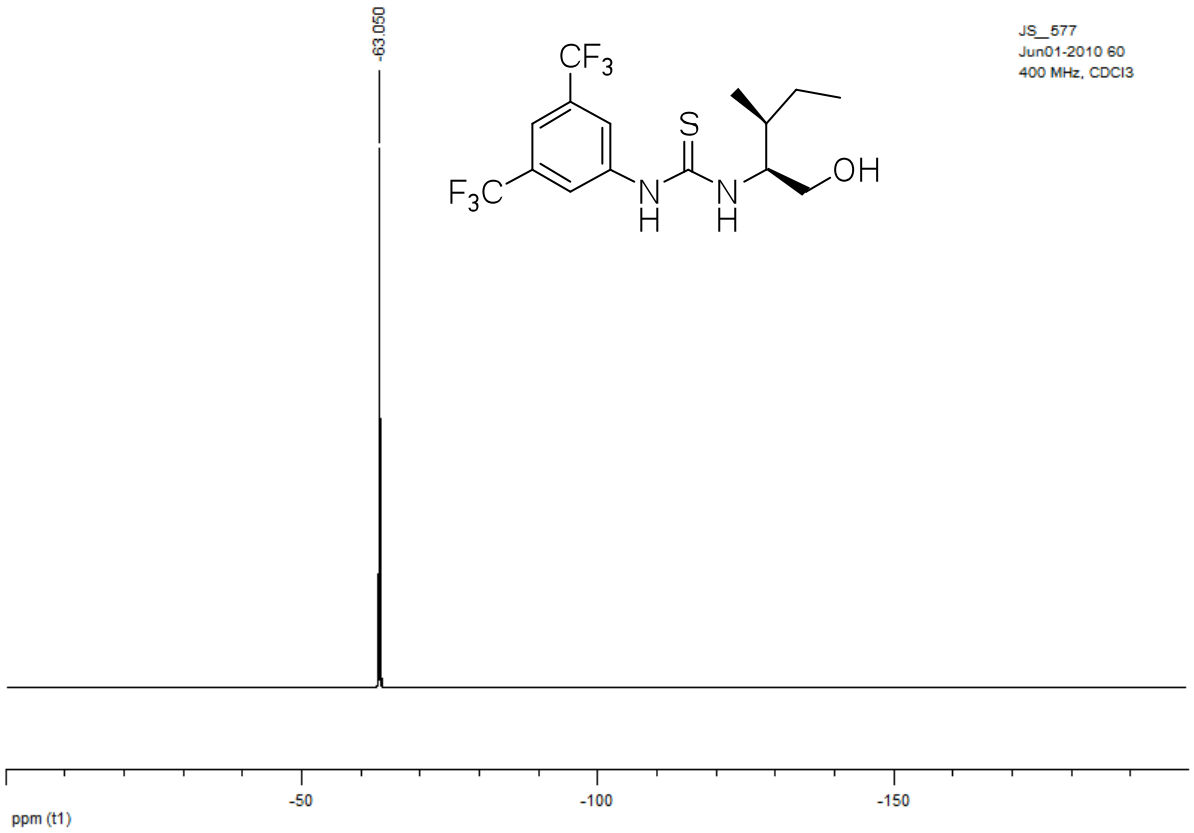

207.247
182.705
143.898
140.521
133.722
133.196
132.669
132.142
131.845
131.162
130.192
128.129
127.523
124.155
123.199
118.874
118.413
118.353
118.295
62.950
59.163
38.006
31.445
31.137
30.830
30.522
30.214
JS_372
MA281S.224
63 MHz, acetone-d6
CF3
S
F3C
N
H
N
H
OH
200
150
100
50
0
ppm (t1)



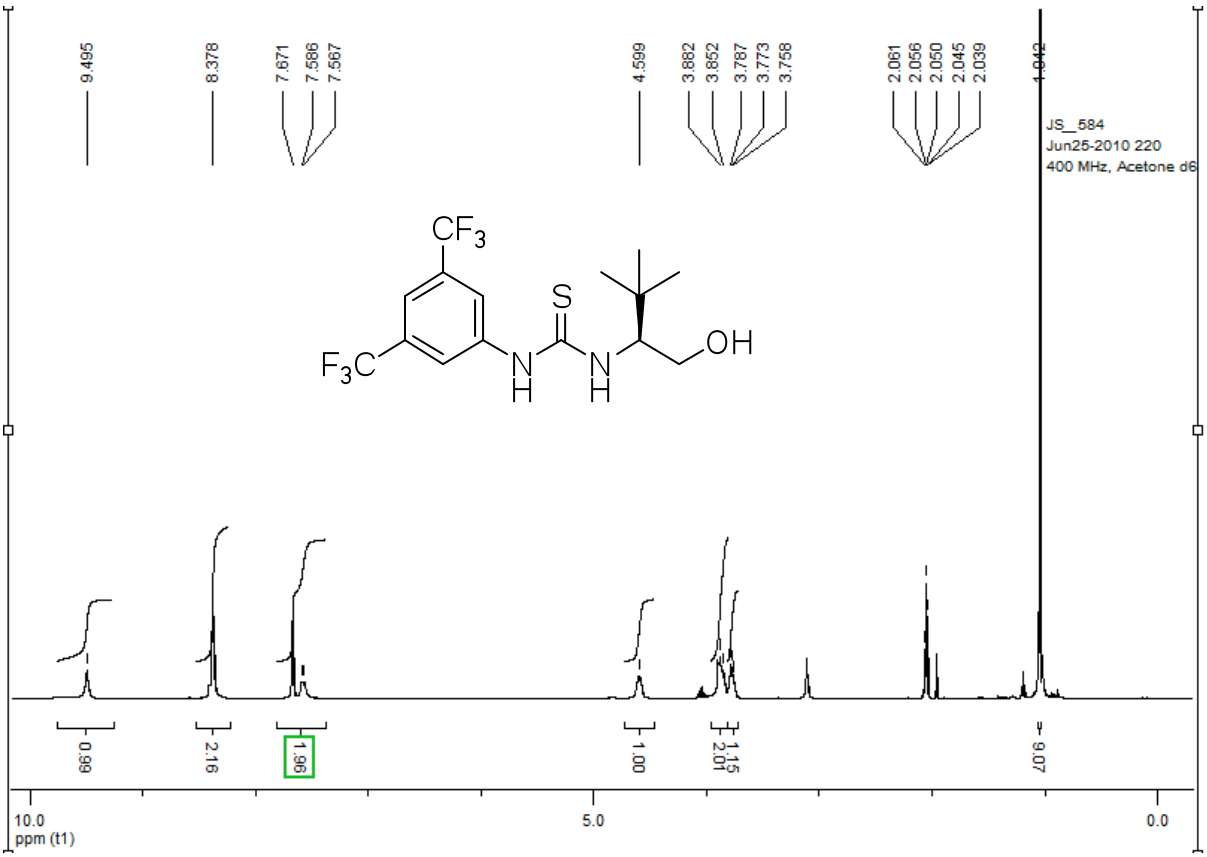
1o

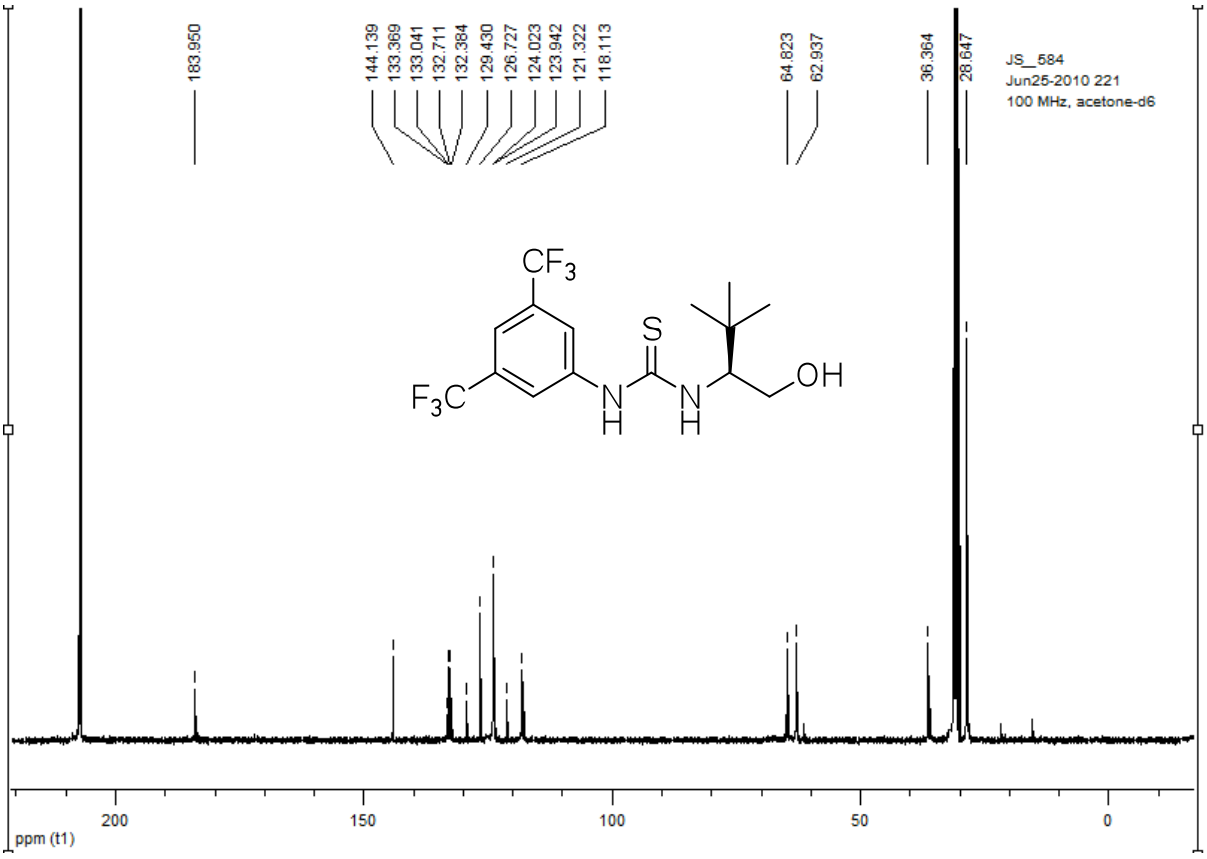

8.964
7.861
7.618
7.260
6.904
6.886
4.502
4.500
3.875
3.853
3.672
3.654
3.644
3.626
3.020
1.649
1.482
1.474
1.463
1.459
1.449
1.440
1.430
1.173
1.158
0.913
0.896
0.878
JS_577
Jun01_2010 60
400 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
0.61
1.94
1.01
1.00
0.60
1.00
1.10
0.57
0.97
1.02
1.04
6.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

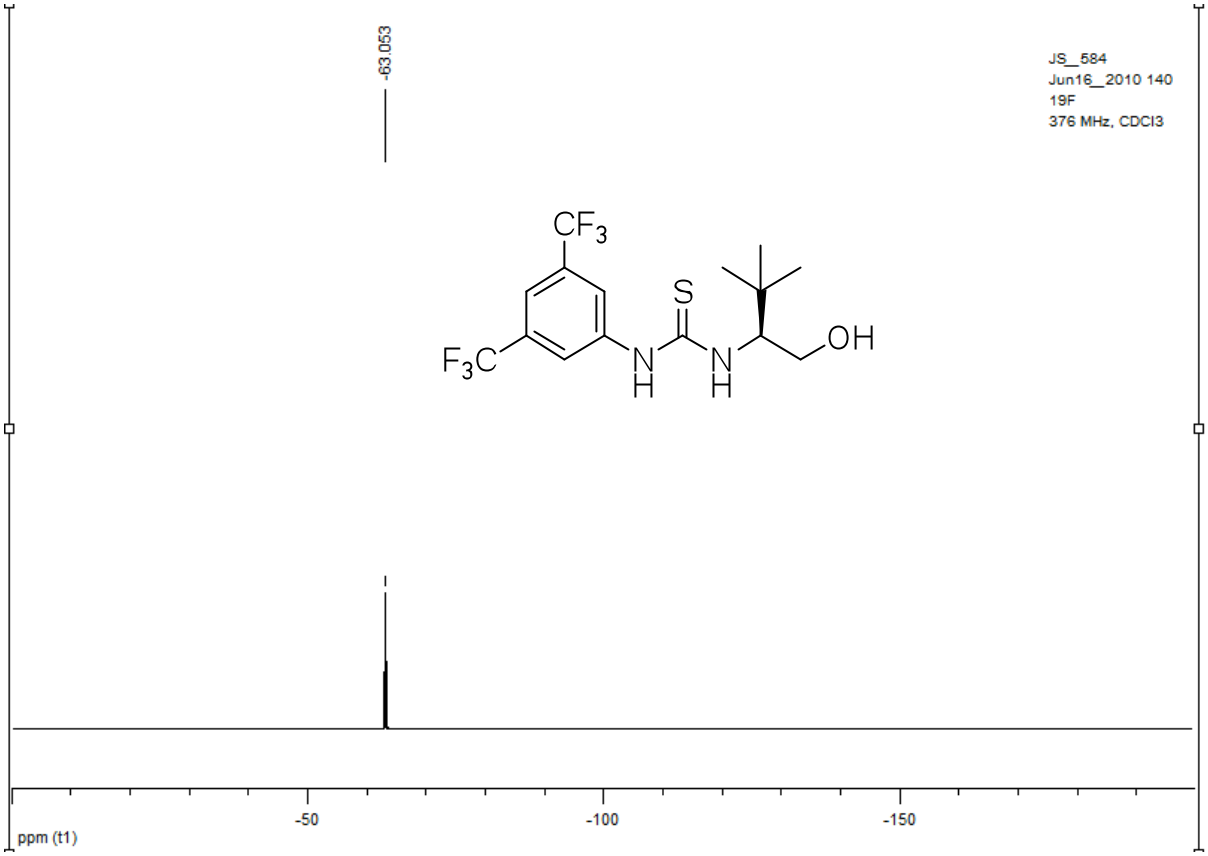

180.994
180.963
139.227
132.440
132.414
126.899
124.190
123.431
121.476
118.769
62.733
62.704
60.472
35.994
25.815
15.338
11.106
JS_577
Jun01-2010 63
100 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
150
100
50
0
ppm (t1)


-63.050
JS_577
Jun01-2010 60
400 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
-50
-100
-150
ppm (t1)

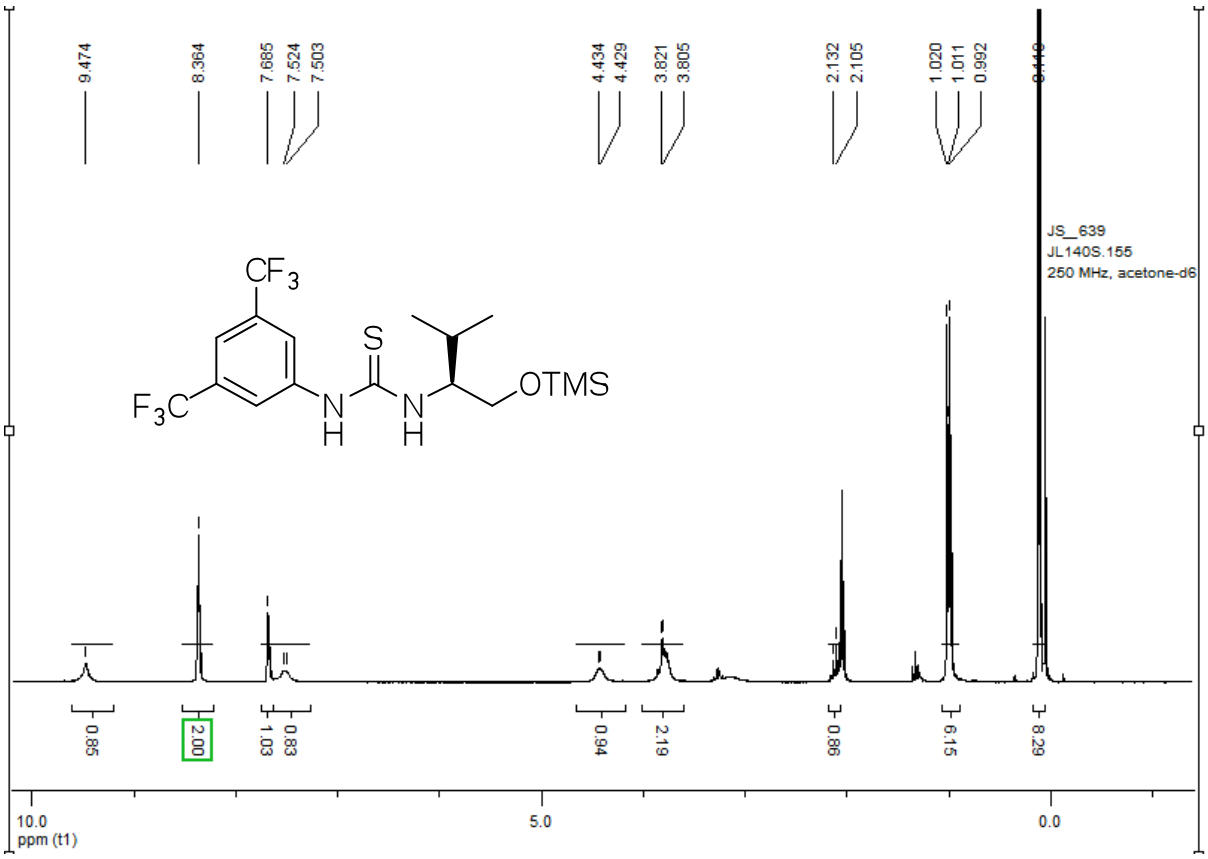
1p

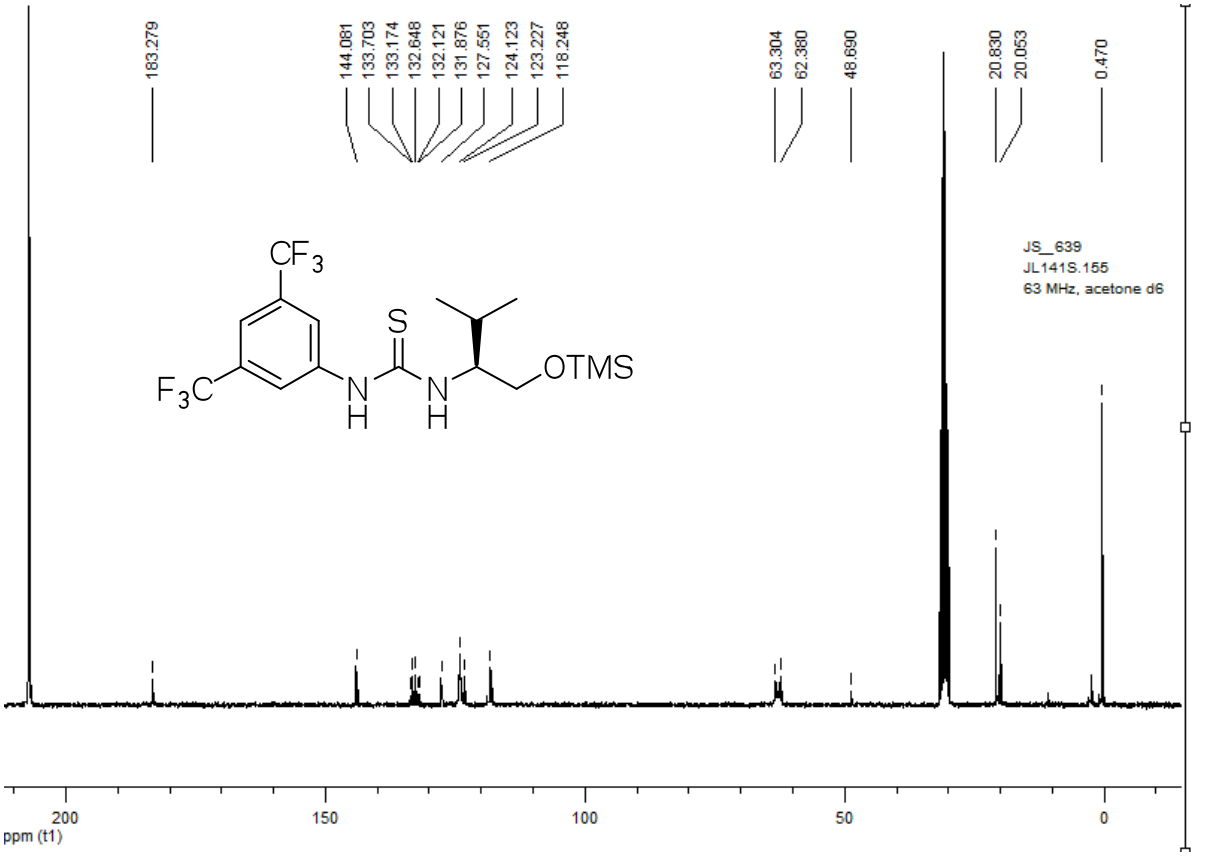

9.495
8.378
7.671
7.586
7.567
4.599
3.882
3.852
3.787
3.773
3.758
2.061
2.056
2.050
2.045
2.039
1.842
JS_584
Jun25-2010 220
400 MHz, Acetone d6
CF3
F3C
S
N
H
N
H
OH
0.99
2.16
1.96
1.00
2.01
1.15
9.07
10.0
ppm (t1)
5.0
0.0

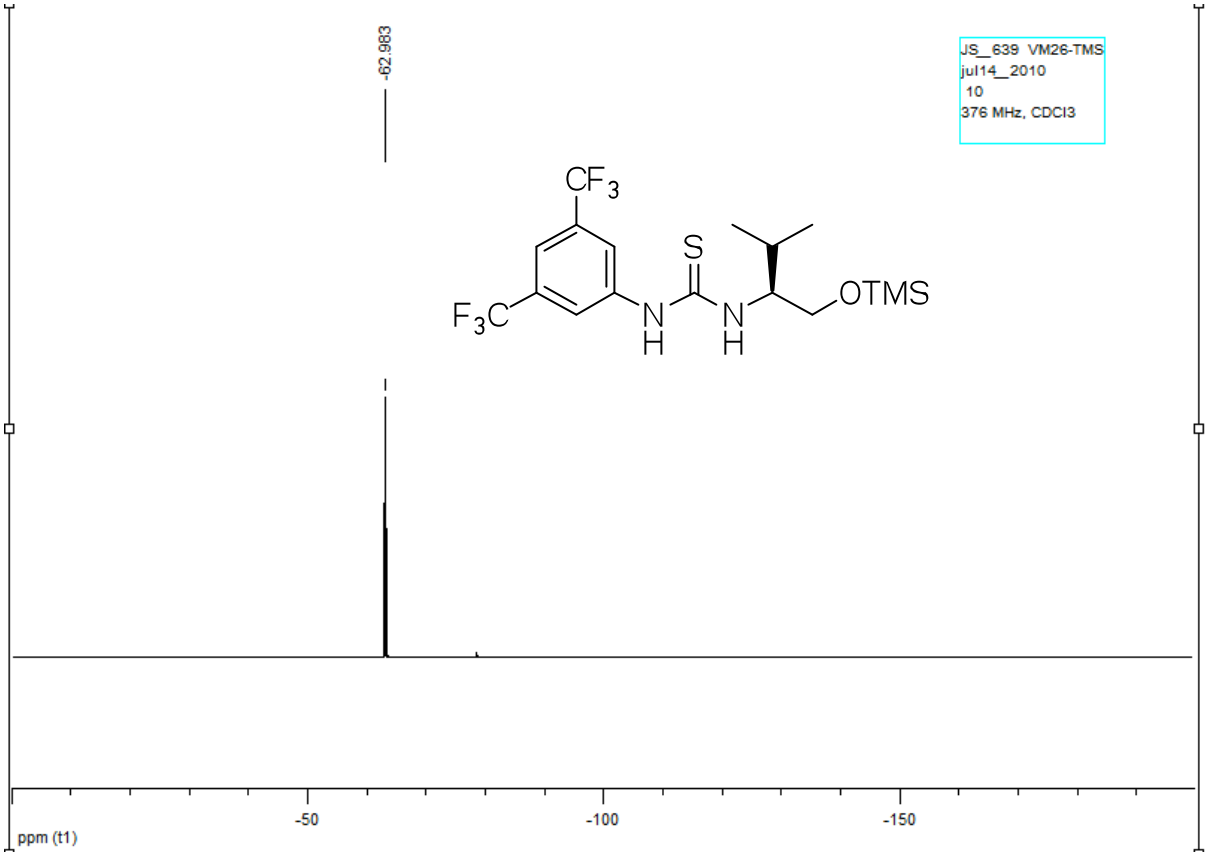

183.950
144.139
133.369
133.041
132.711
132.384
129.430
126.727
124.023
123.942
121.322
118.113
64.823
62.937
36.364
28.647
JS_584
Jun25-2010 221
100 MHz, acetone-d6
CF3
F3C
S
N
H
N
H
OH
200
150
100
50
0
ppm (t1)


-63.053
JS_584
Jun16_2010 140
19F
376 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OH
-50
-100
-150
ppm (t1)

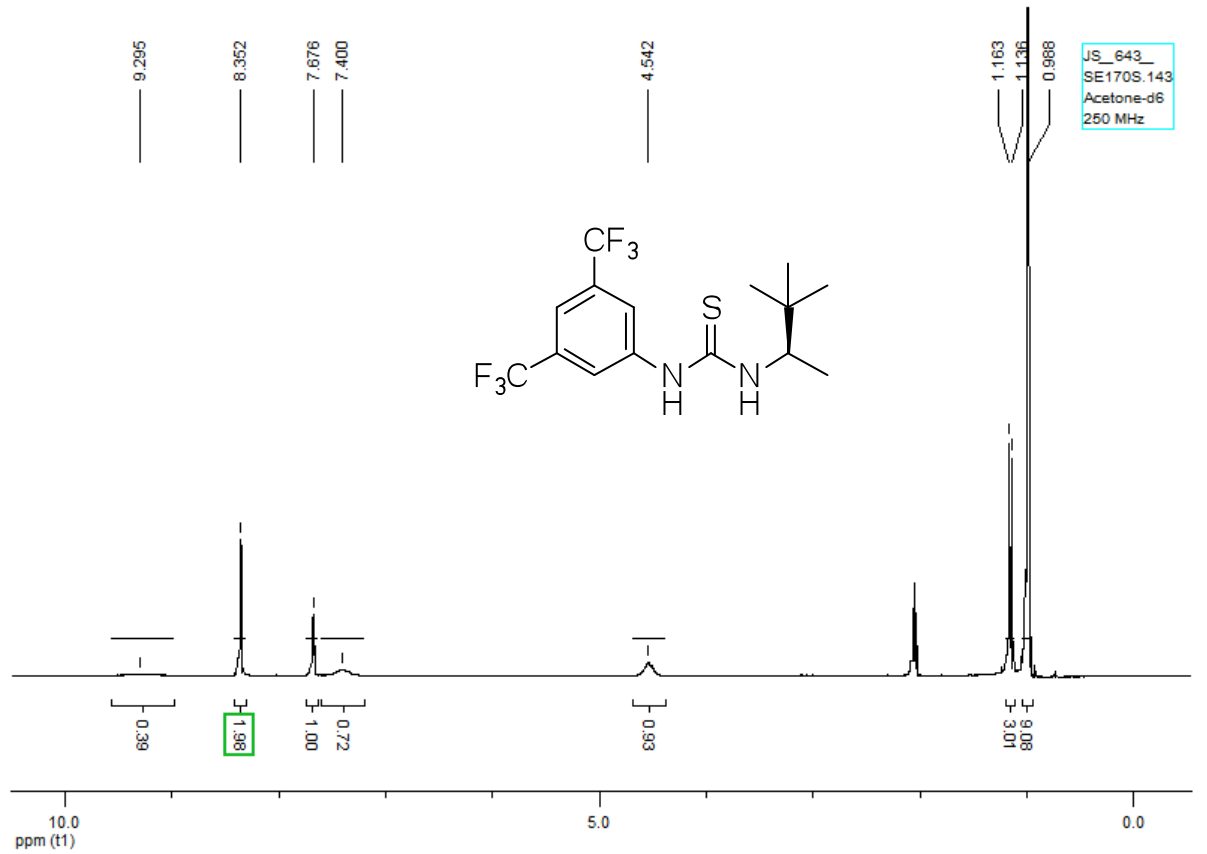
7

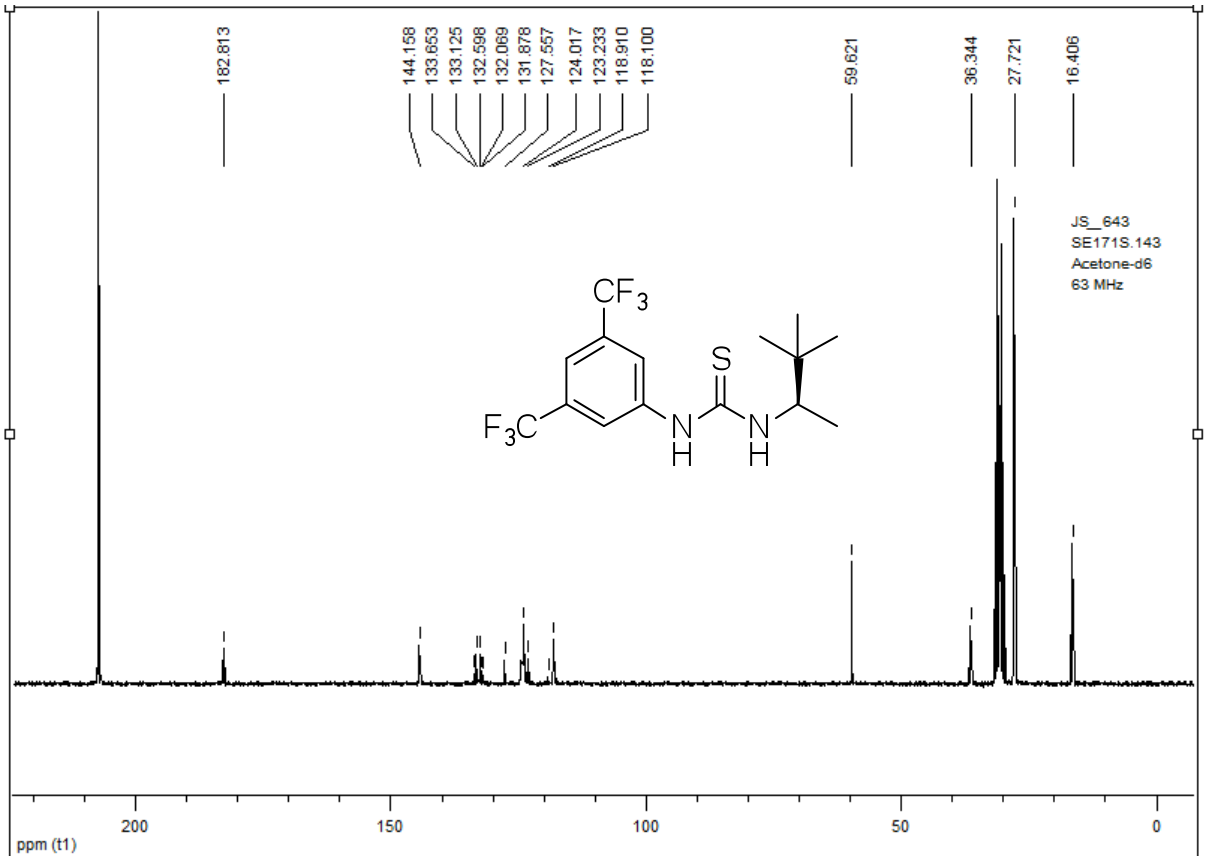

9.474
8.364
7.685
7.524
7.503
4.434
4.429
3.821
3.805
2.132
2.105
1.020
1.011
0.992
8.448
JS_639
JL140S.155
250 MHz, acetone-d6
CF3
F3C
S
N
H
N
H
OTMS
0.85
2.00
1.03
0.83
0.94
2.19
0.86
9.15
8.29
10.0
ppm (t1)
5.0
0.0


183.279
144.081
133.703
133.174
132.648
132.121
131.876
127.551
124.123
123.227
118.248
63.304
62.380
48.690
20.830
20.053
0.470
JS_639
JL141S.155
63 MHz, acetone d6
CF3
F3C
S
N
H
N
H
OTMS
200
ppm (t1)
150
100
50
0


-62.983
JS_639 VM26-TMS
jul14_2010
10
376 MHz, CDCl3
CF3
F3C
S
N
H
N
H
OTMS
-50
-100
-150
ppm (t1)

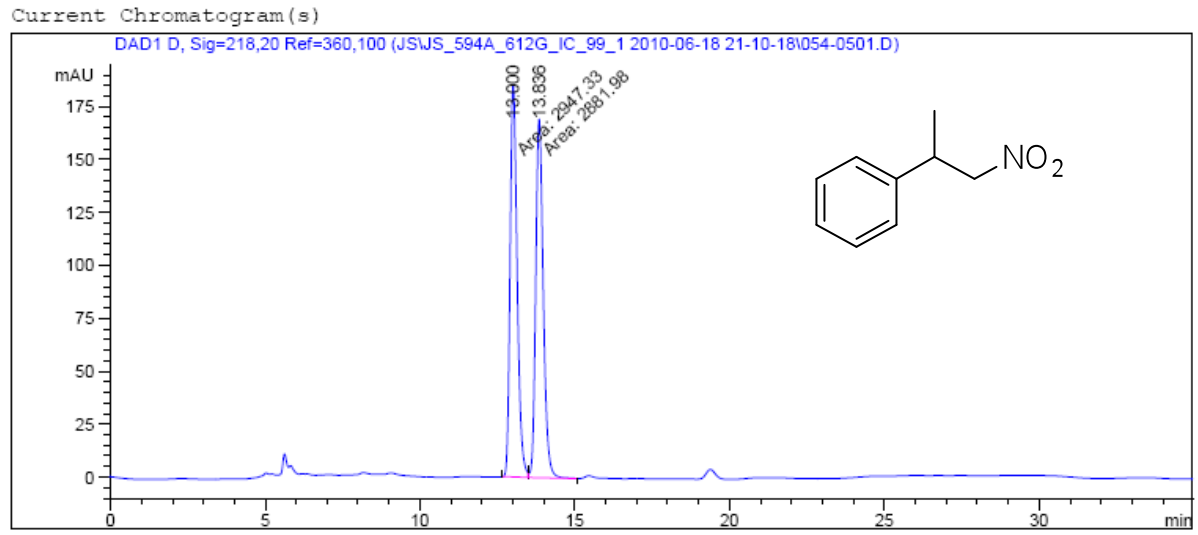
8

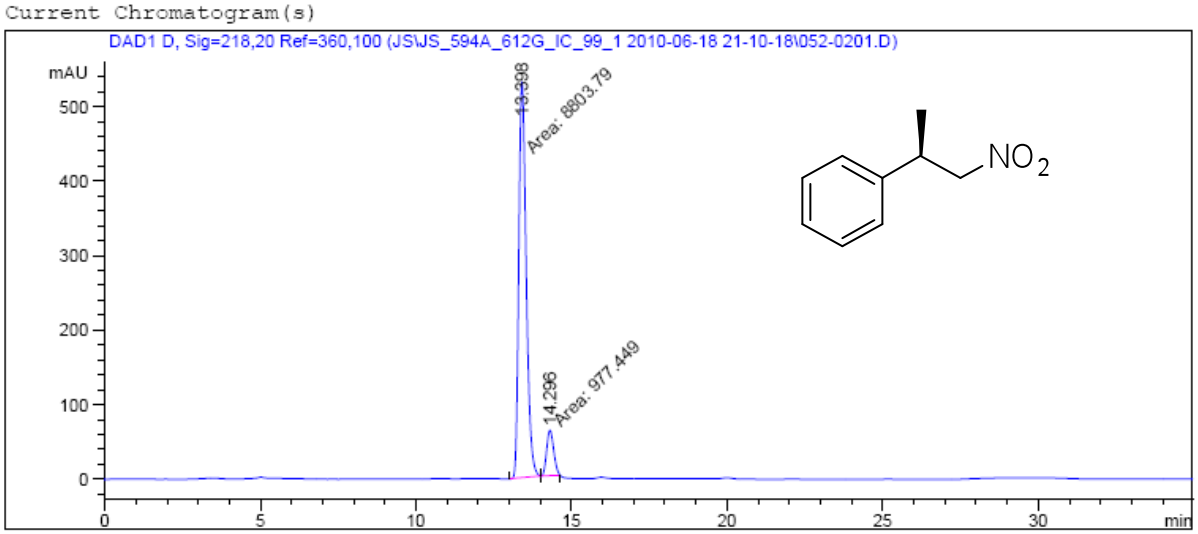

9.295
8.352
7.676
7.400
4.542
1.163
1.136
0.988
JS_643_
SE170S.143
Acetone-d6
250 MHz
CF3
F3C
S
N
H
N
H
0.39
1.98
1.00
0.72
0.93
3.01
9.08
10.0
5.0
0.0
ppm (t1)


182.813
144.158
133.653
133.125
132.598
132.069
131.878
127.557
124.017
123.233
118.910
118.100
59.621
36.344
27.721
16.406
JS_643
SE171S.143
Acetone-d6
63 MHz
CF3
F3C
S
N
H
N
H
200
150
100
50
0
ppm (t1)

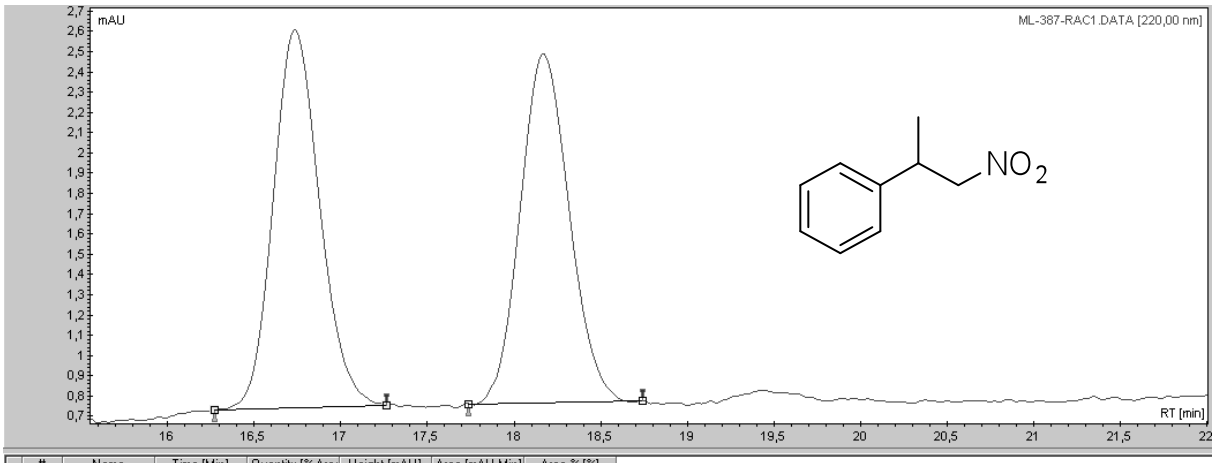
3.2. HPLC data

4a



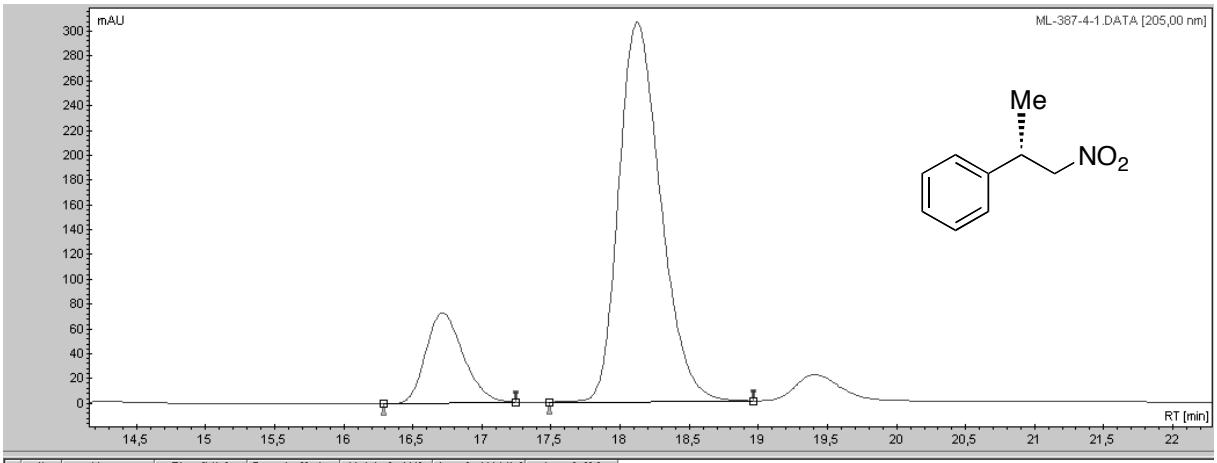


rac-4a (Varian HPLC)



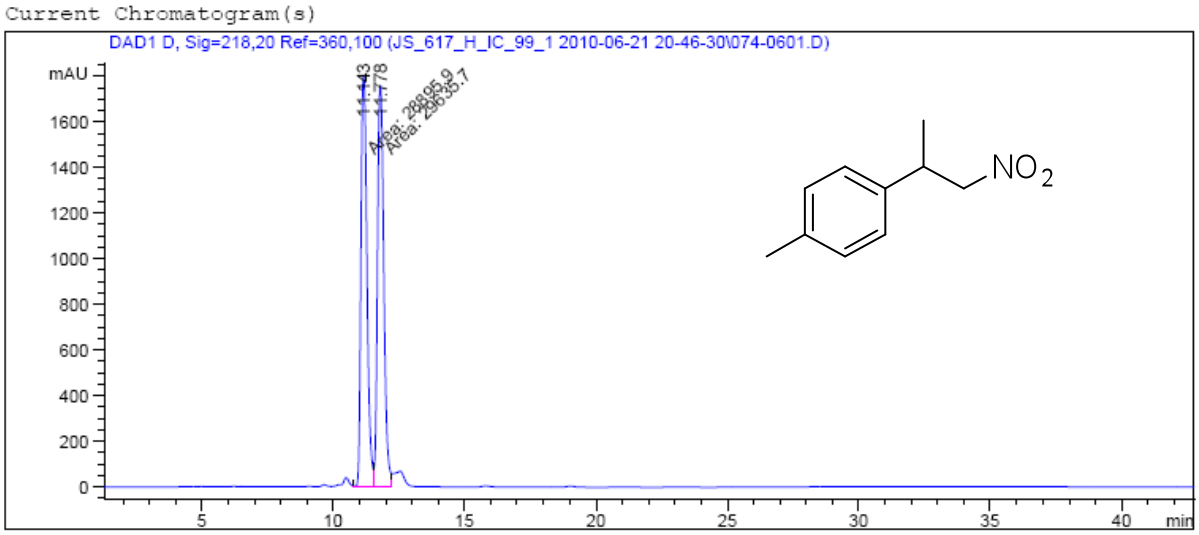
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	16,73	50,77	1,9	0,6	50,768
2	UNKNOWN	18,16	49,23	1,7	0,6	49,232
Total			100,00	3,6	1,1	100,000

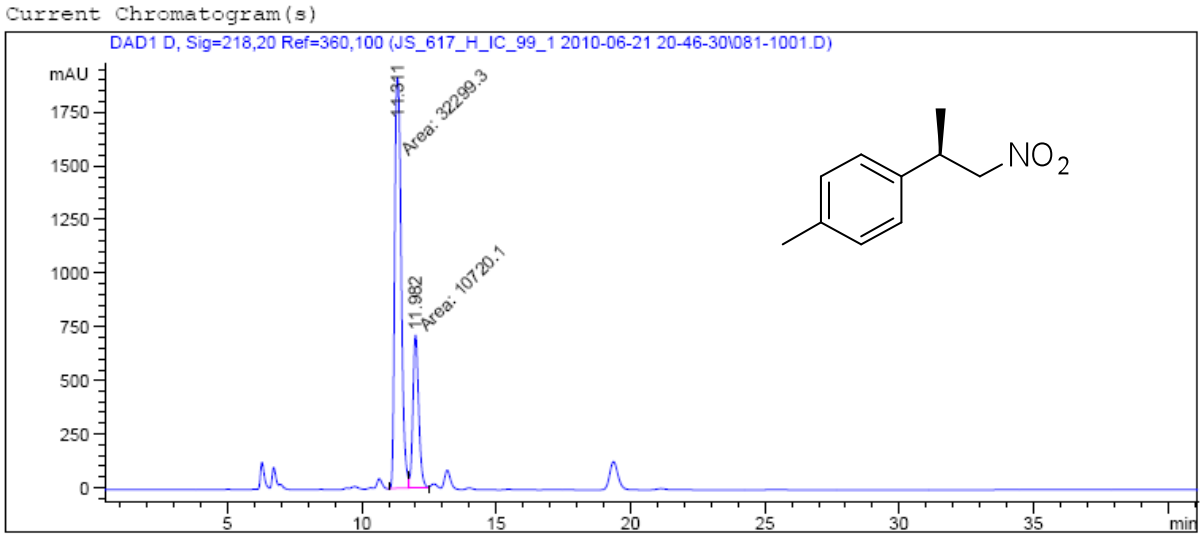
ent-4a (Varian HPLC)



#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	16,72	17,57	72,7	22,8	17,566
2	UNKNOWN	18,12	82,43	305,6	107,1	82,434
Total			100,00	378,3	130,0	100,000

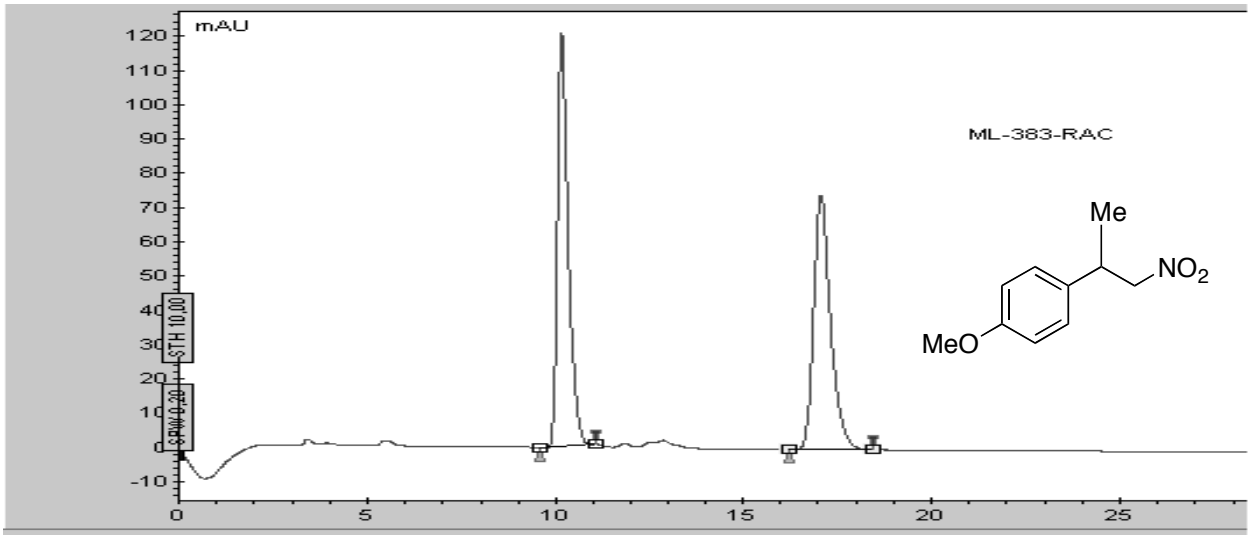
4b


Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS_617_H_IC_99_1 2010-06-21 20-46-30\074-0601.D)
mAU
11.143
11.778
Area: 28895.9
Area: 29635.7
NO2
min


Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS_617_H_IC_99_1 2010-06-21 20-46-30\081-1001.D)
mAU
11.911
Area: 32299.3
11.982
Area: 10720.1
NO2
min

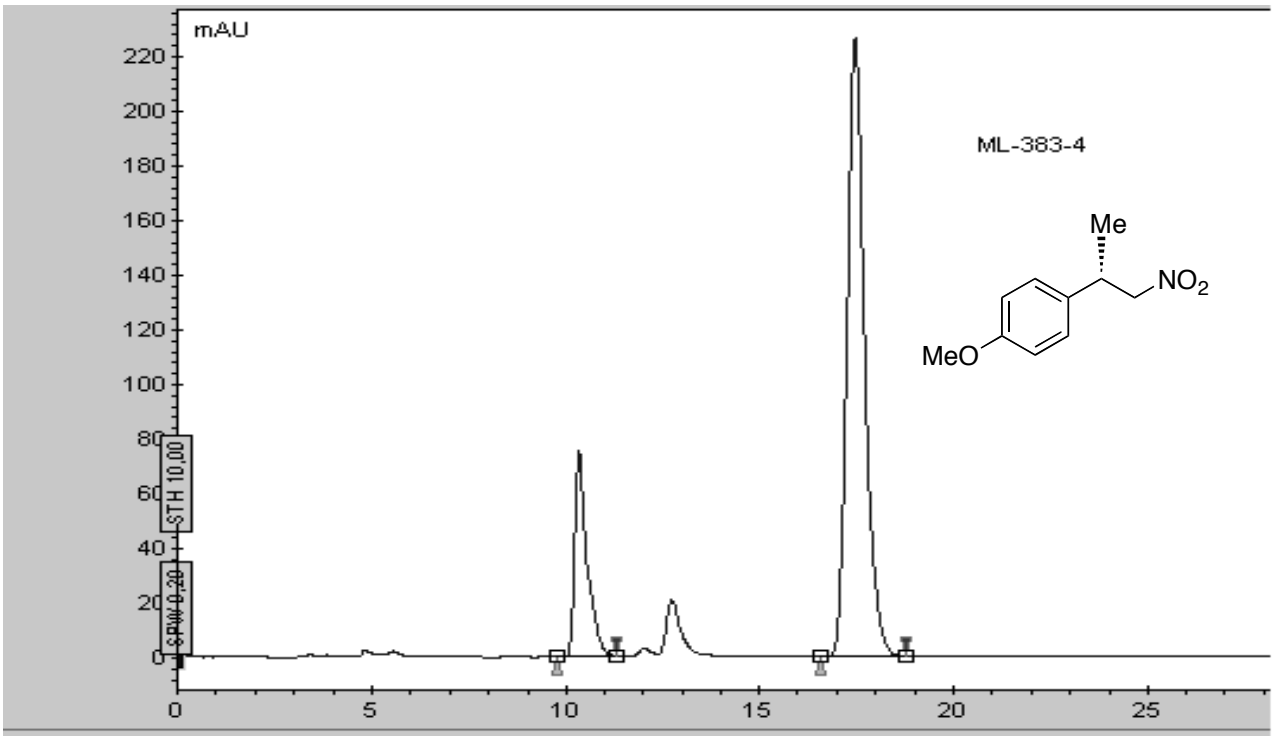
4c

rac-**4c (Varian HPLC)**



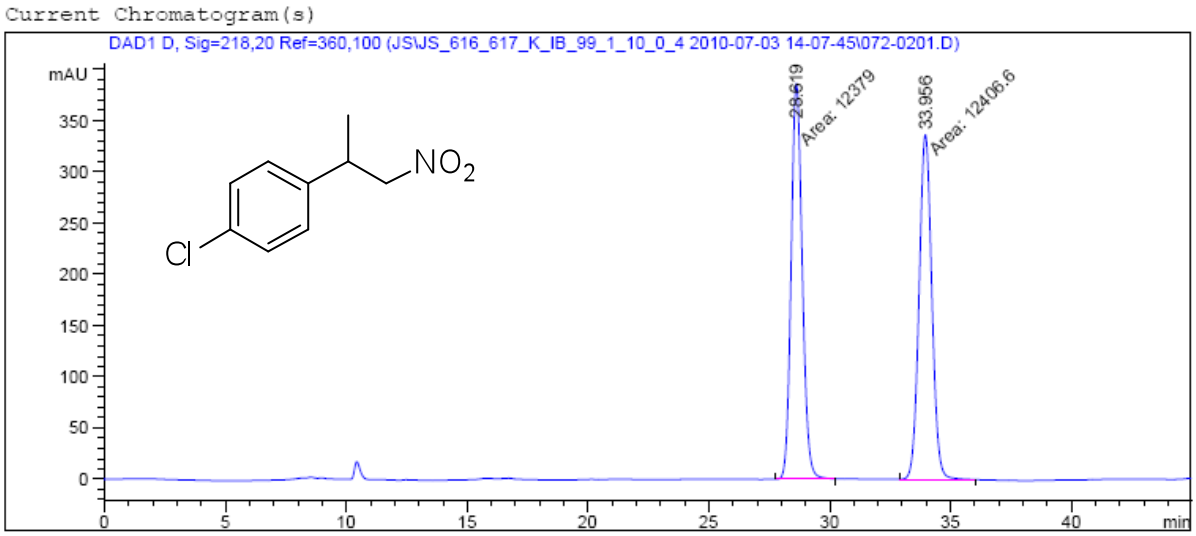
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	10,17	50,62	120,3	39,5	50,621
2	UNKNOWN	17,07	49,38	74,2	38,6	49,379
Total			100,00	194,6	78,1	100,000

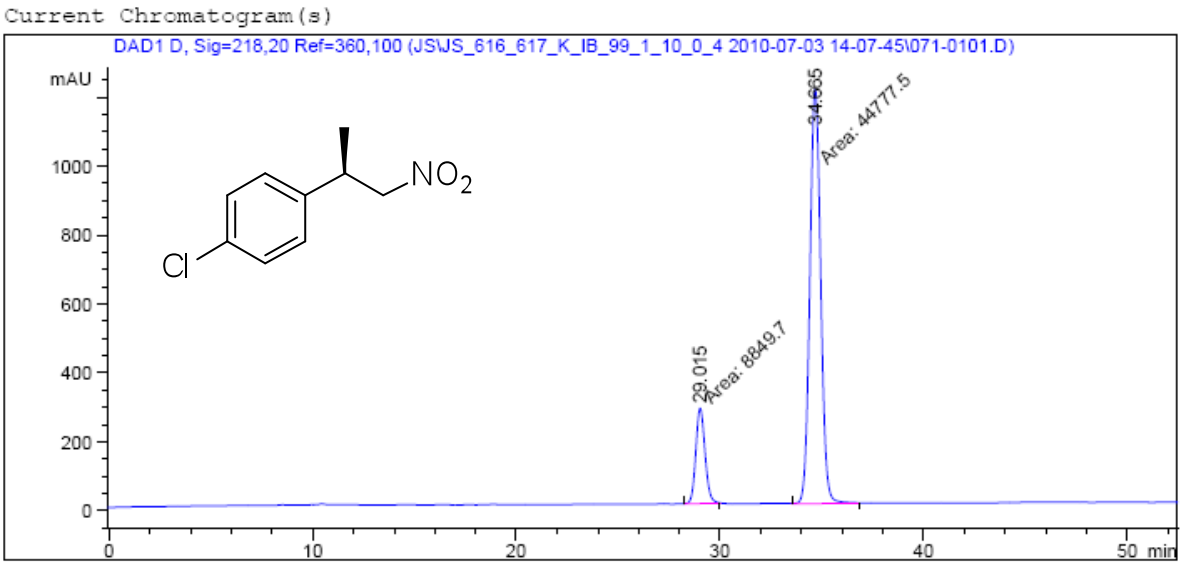
(*R*)-**4c**



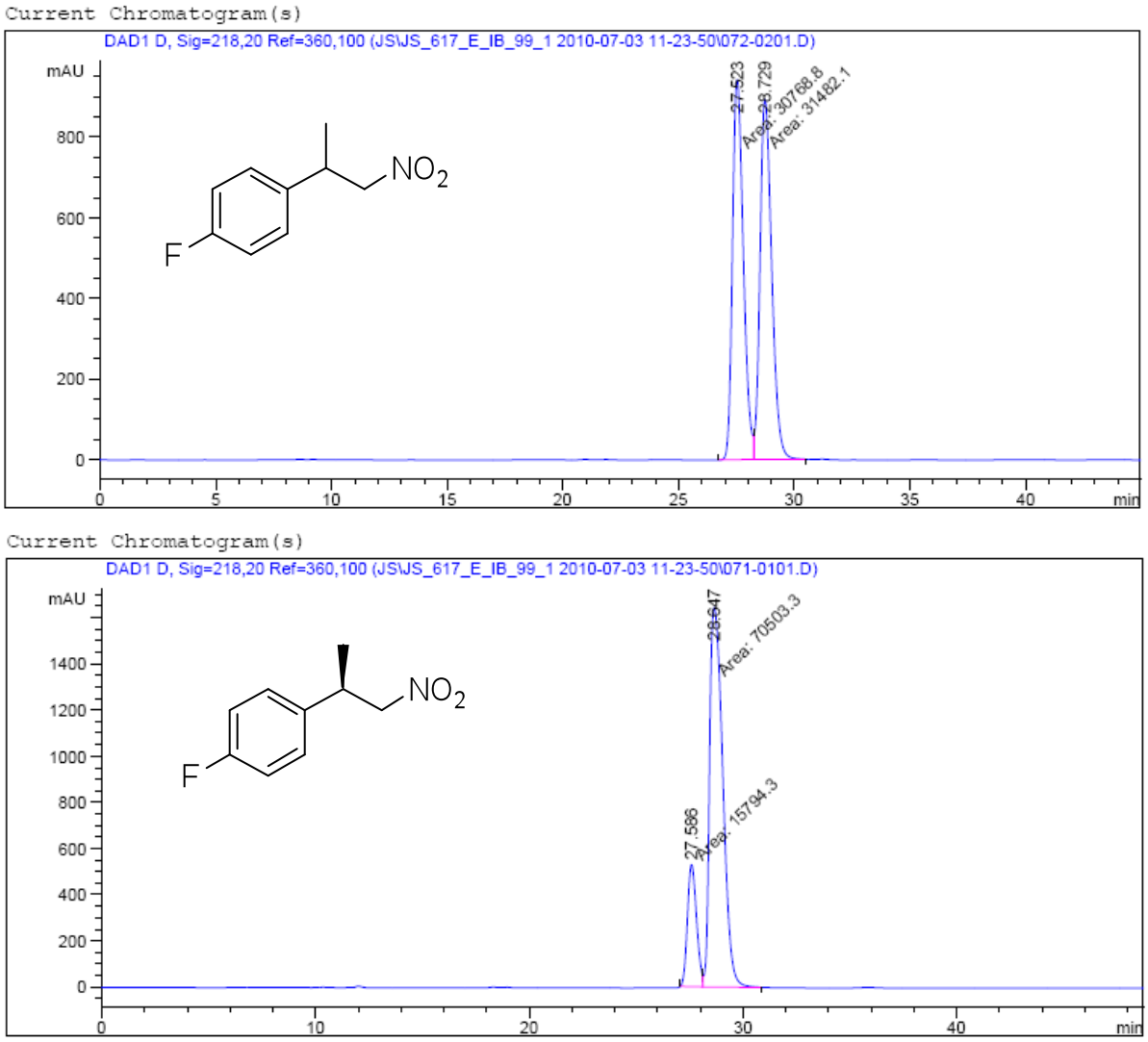
#	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	10,35	19,17	75,4	27,9	19,168
2	UNKNOWN	17,47	80,83	226,4	117,4	80,832
Total			100,00	301,8	145,3	100,000

4d

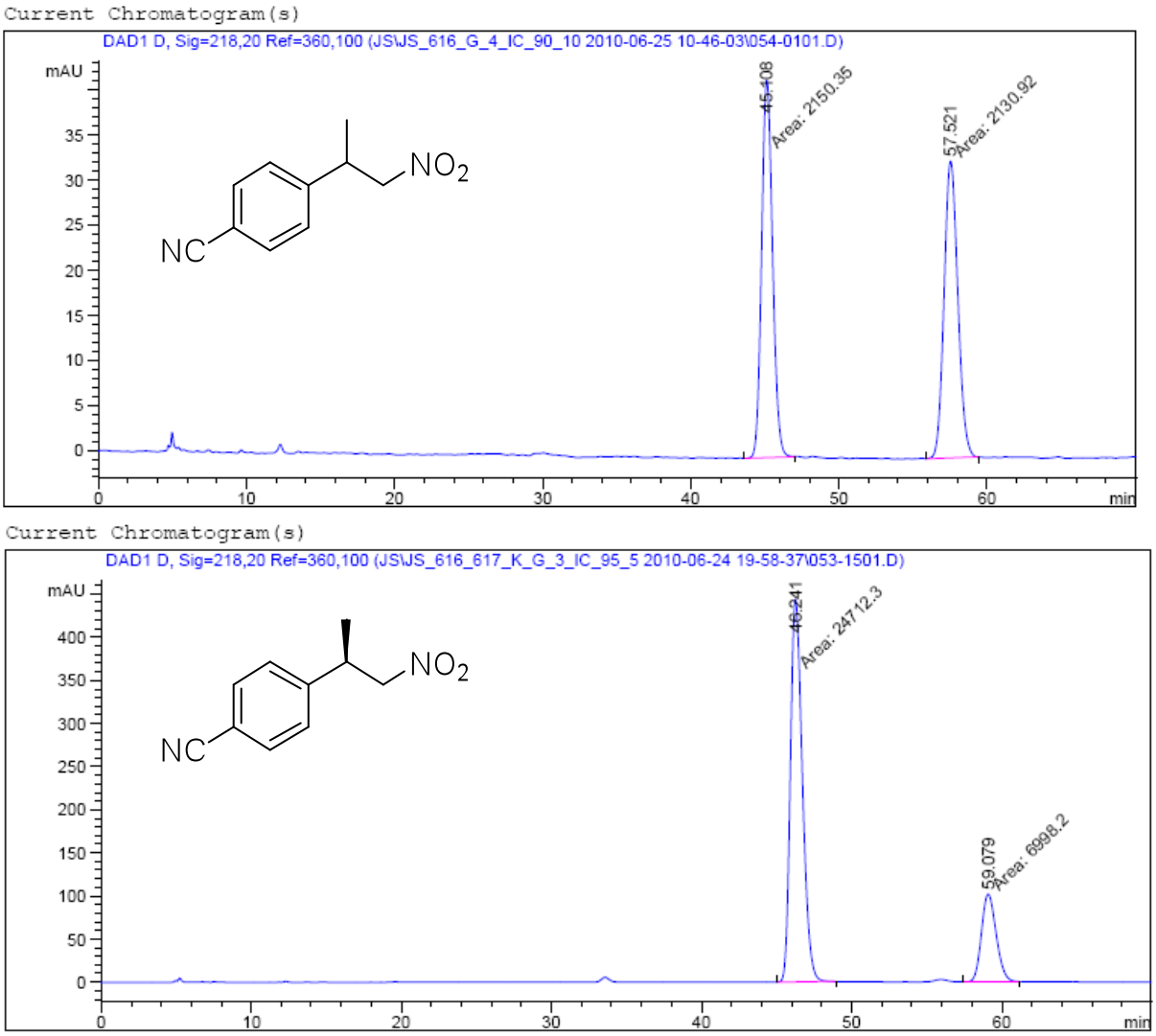

Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_616_617_K_IB_99_1_10_0_4 2010-07-03 14-07-45\072-0201.D)
mAU
350
300
250
200
150
100
50
0
28.619
Area: 12379
33.956
Area: 12406.6
NO2
Cl
0
5
10
15
20
25
30
35
40
min


Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_616_617_K_IB_99_1_10_0_4 2010-07-03 14-07-45\071-0101.D)
mAU
1000
800
600
400
200
0
29.015
Area: 8849.7
34.665
Area: 44777.5
NO2
Cl
0
10
20
30
40
50 min

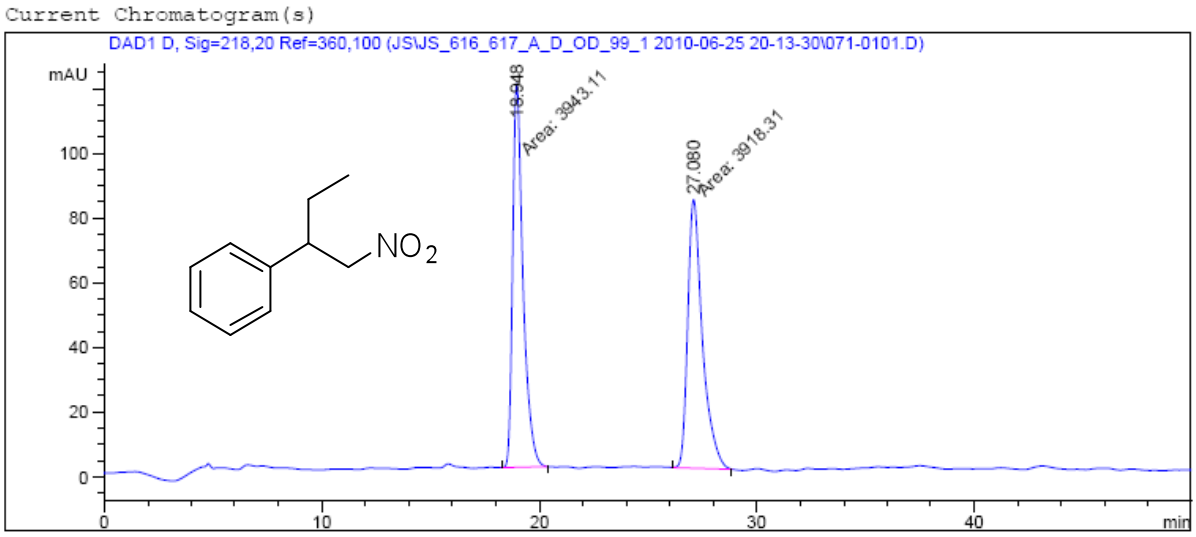
4e

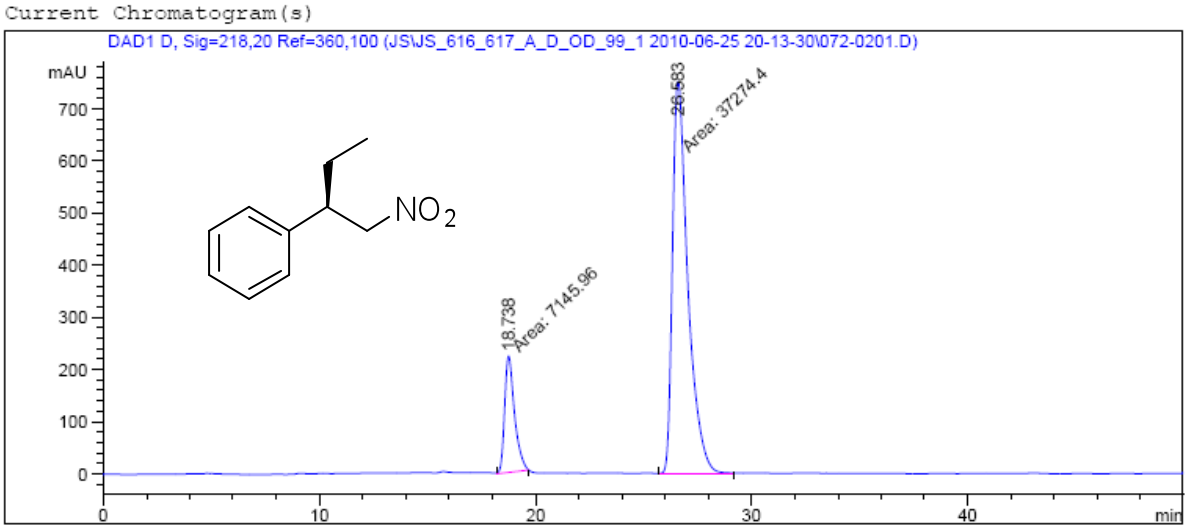

Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_617_E_IB_99_1 2010-07-03 11-23-50\072-0201.D)
mAU
800
600
400
200
0
27.523
Area: 30768.8
28.729
Area: 31482.1
NO2
F
0
5
10
15
20
25
30
35
40
min
Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_617_E_IB_99_1 2010-07-03 11-23-50\071-0101.D)
mAU
1400
1200
1000
800
600
400
200
0
28.647
Area: 70503.3
27.586
Area: 15794.3
NO2
F
0
10
20
30
40
min

4f

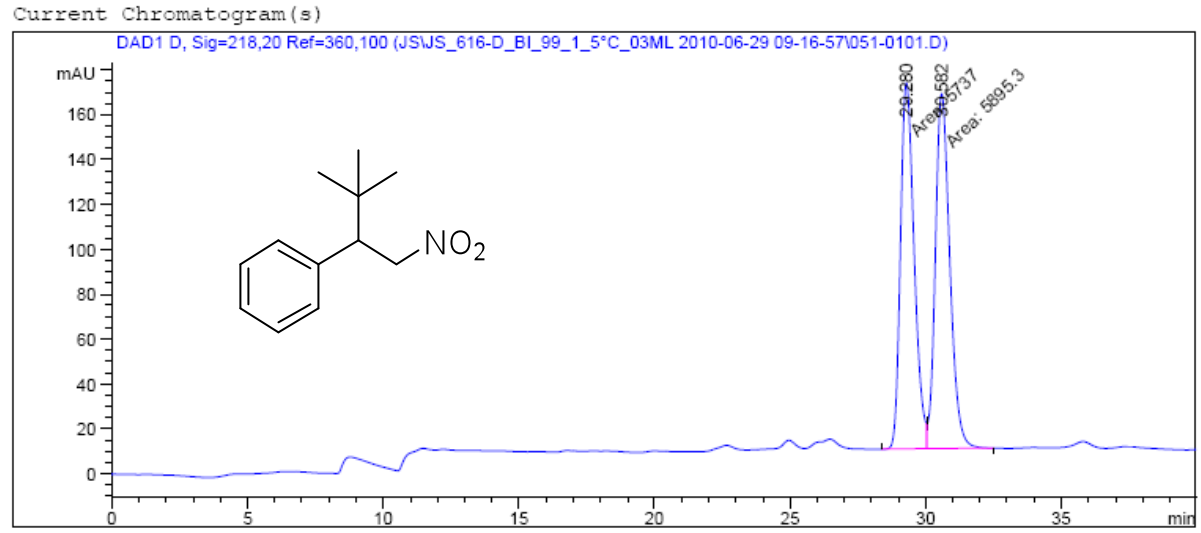

Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_616_G_4_IC_90_10 2010-06-25 10-46-03\054-0101.D)
mAU
45.108
Area: 2150.35
57.521
Area: 2130.92
NC
NO2
min
Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_616_617_K_G_3_IC_95_5 2010-06-24 19-58-37\053-1501.D)
mAU
46.241
Area: 24712.3
59.079
Area: 6998.2
NC
NO2
min

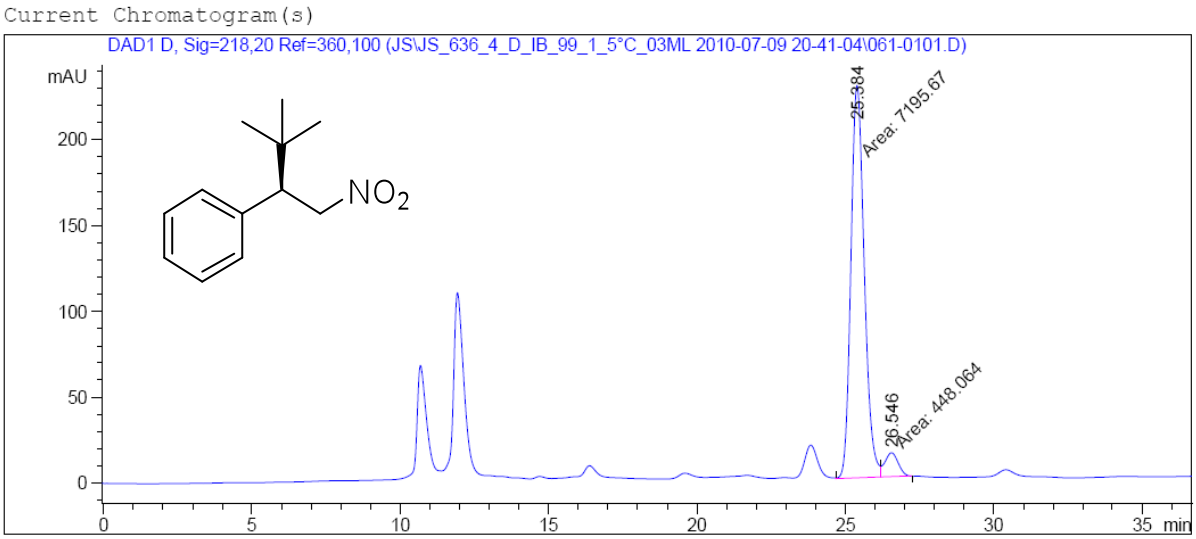
4g


Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_616_617_A_D_OD_99_1 2010-06-25 20-13-30\071-0101.D)
mAU
18.948
Area: 3943.11
27.080
Area: 3918.31
NO2
0
20
40
60
80
100
0
10
20
30
40
min

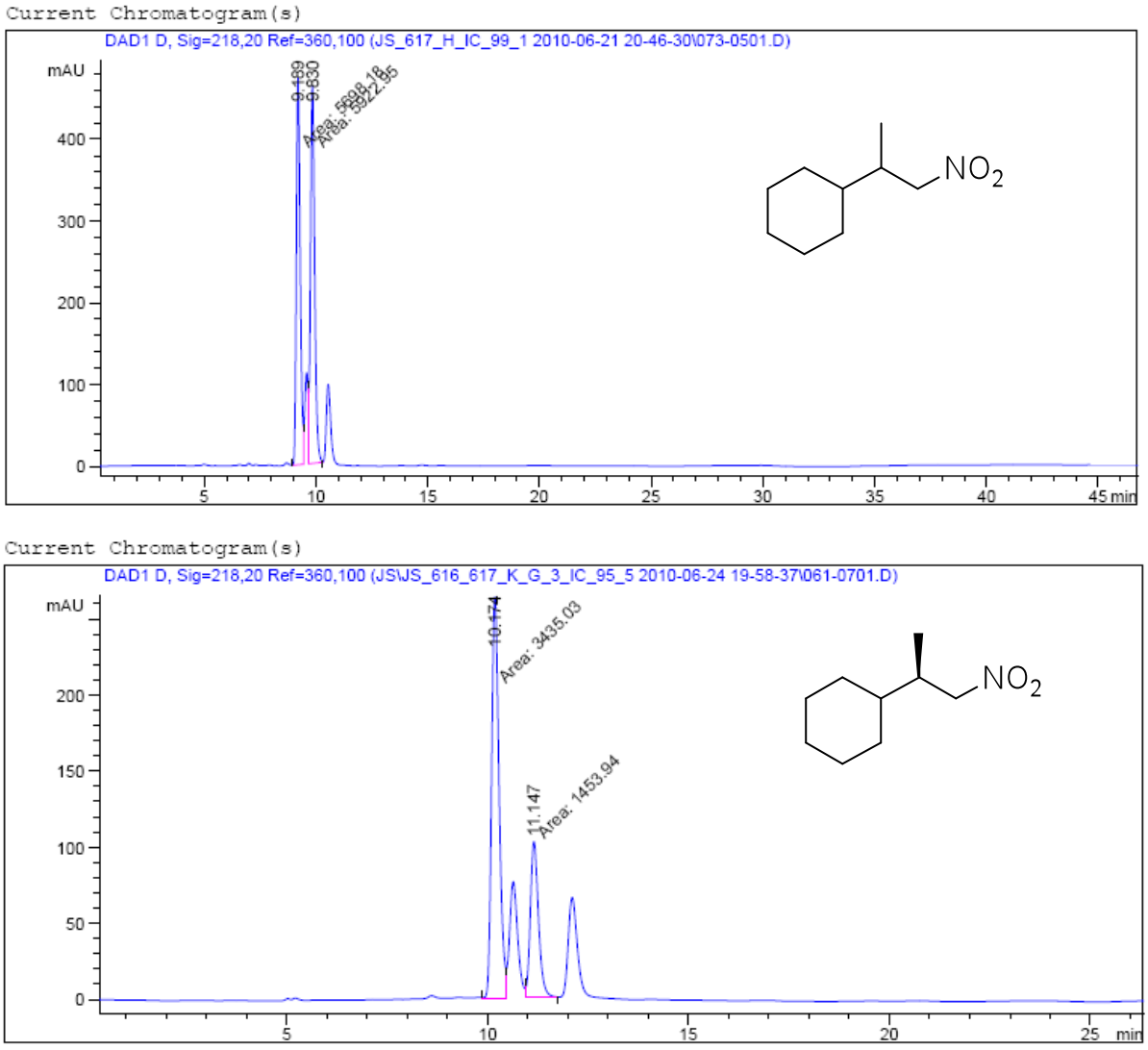

Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_616_617_A_D_OD_99_1 2010-06-25 20-13-30\072-0201.D)
mAU
18.738
Area: 7145.96
26.683
Area: 37274.4
NO2
0
100
200
300
400
500
600
700
0
10
20
30
40
min

4h

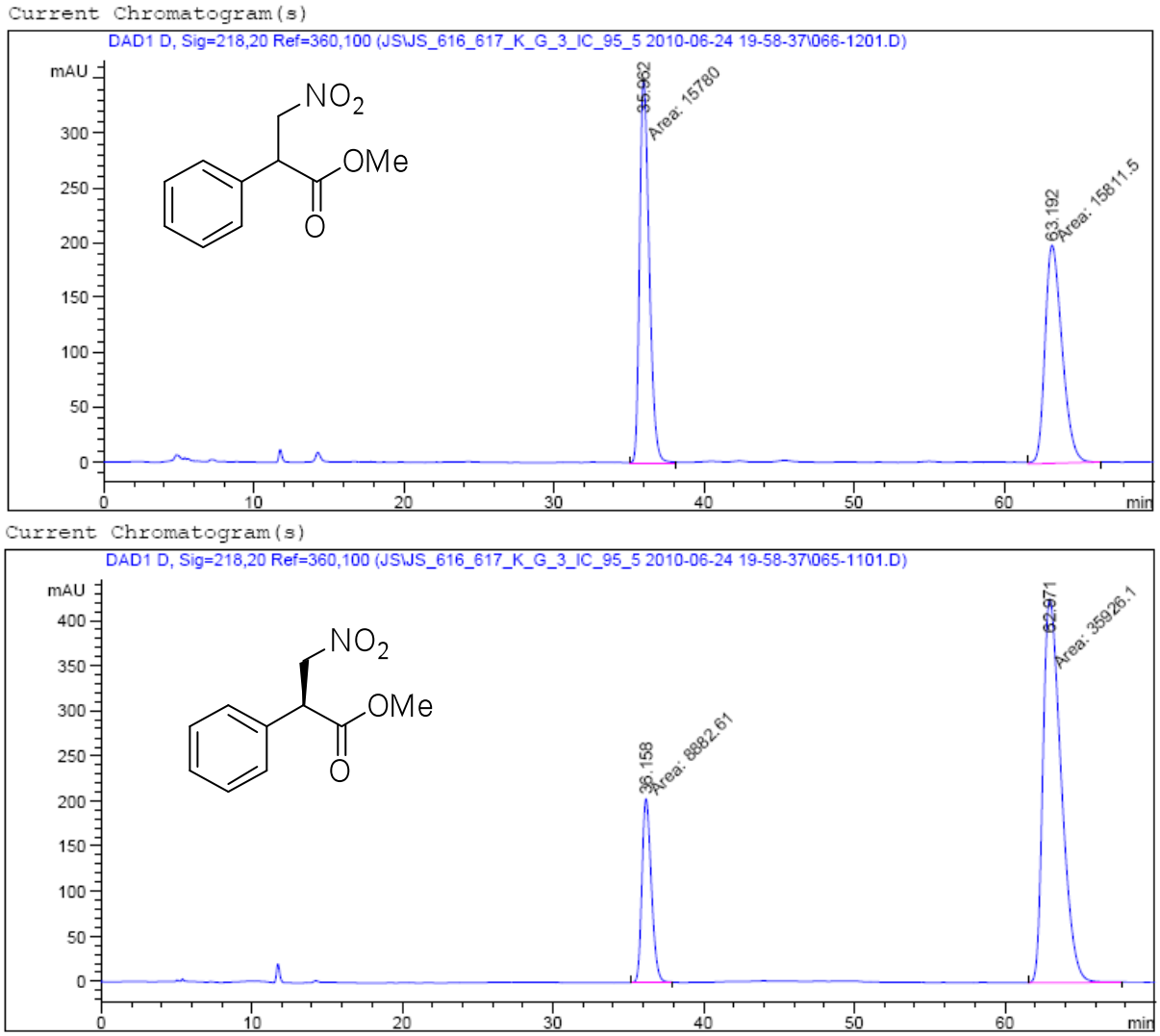

Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_616-D_BI_99_1_5°C_03ML 2010-06-29 09-16-57\051-0101.D)
mAU
NO2
Area: 5895.3
min


Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_636_4_D_IB_99_1_5°C_03ML 2010-07-09 20-41-04\061-0101.D)
mAU
NO2
25.384
Area: 7195.67
26.546
Area: 448.064
min

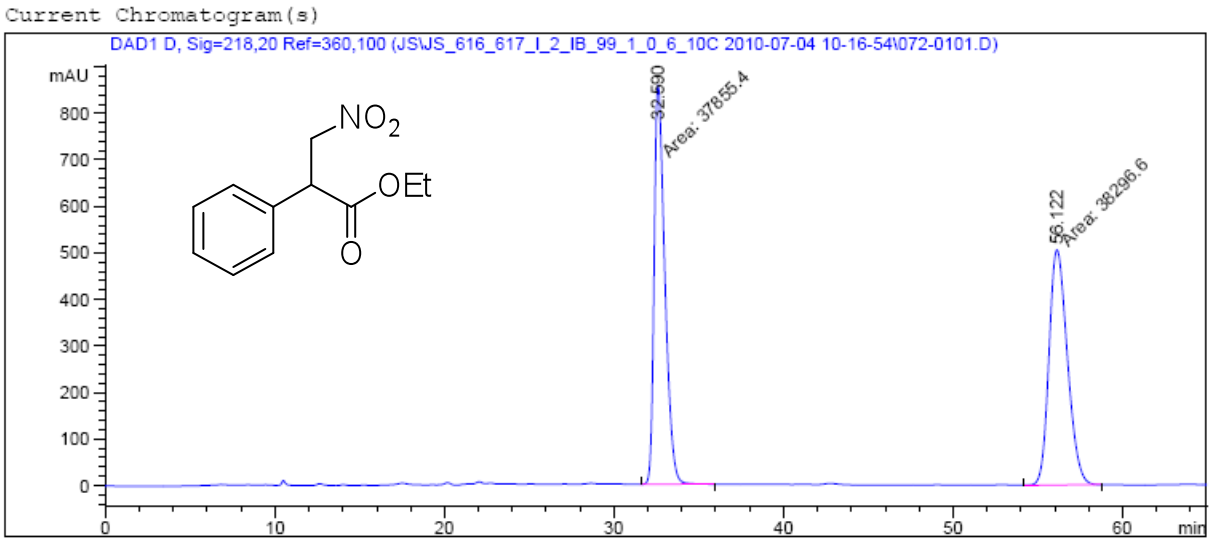
4i

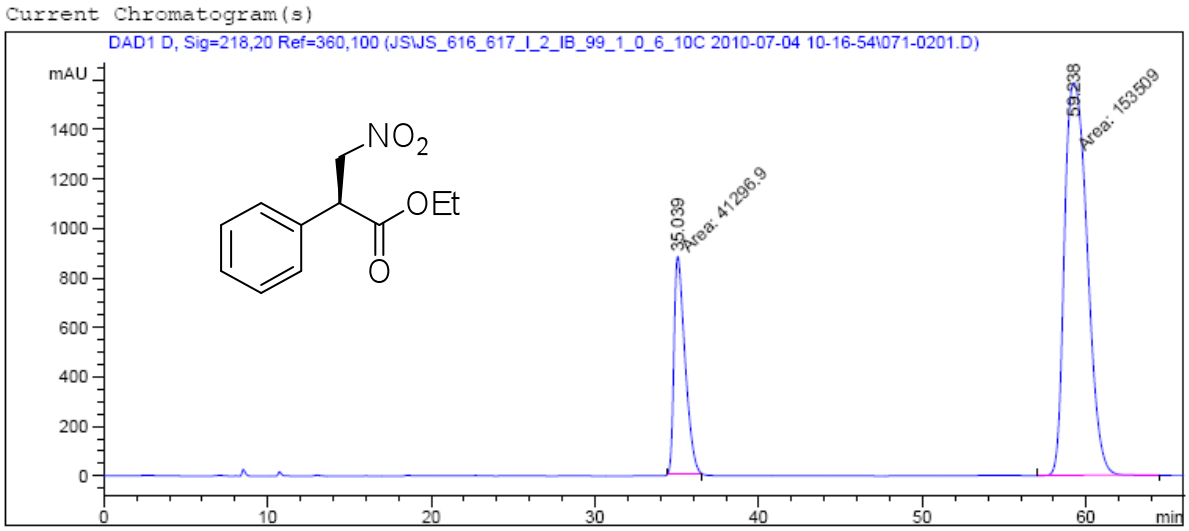

Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS_617_H_IC_99_1 2010-06-21 20-46-30\073-0501.D)
mAU
9.169
9.830
Area: 5698.18
Area: 3922.85
NO2
Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_616_617_K_G_3_IC_95_5 2010-06-24 19-58-37\061-0701.D)
mAU
10.774
Area: 3435.03
11.147
Area: 1453.94
NO2
min

6a

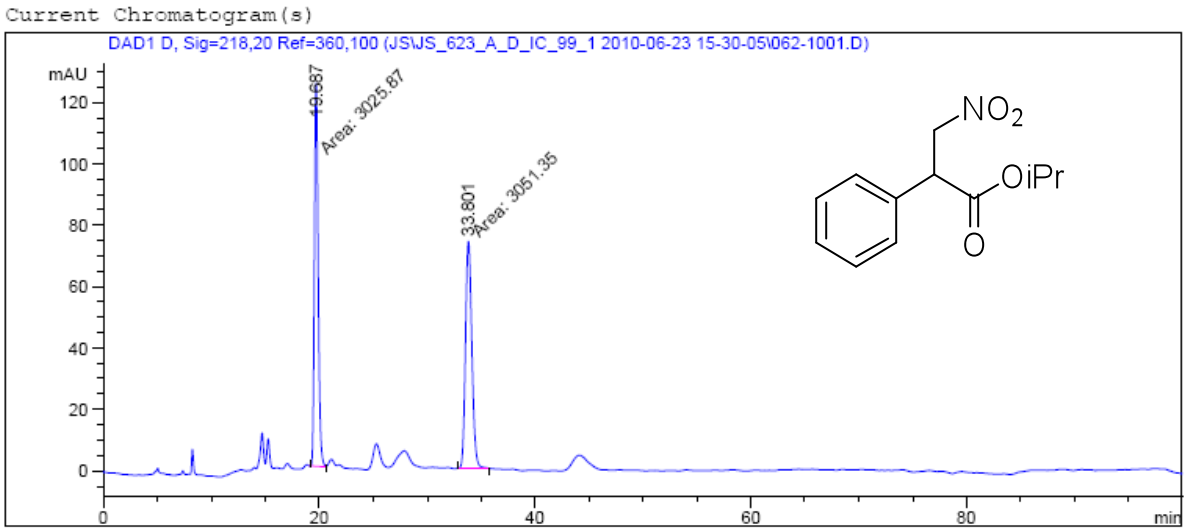

Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_616_617_K_G_3_IC_95_5 2010-06-24 19-58-37\066-1201.D)
mAU
NO2
OMe
O
35.962
Area: 15780
63.192
Area: 15811.5
min
Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_616_617_K_G_3_IC_95_5 2010-06-24 19-58-37\065-1101.D)
mAU
NO2
OMe
O
36.158
Area: 8882.61
62.971
Area: 35926.1
min

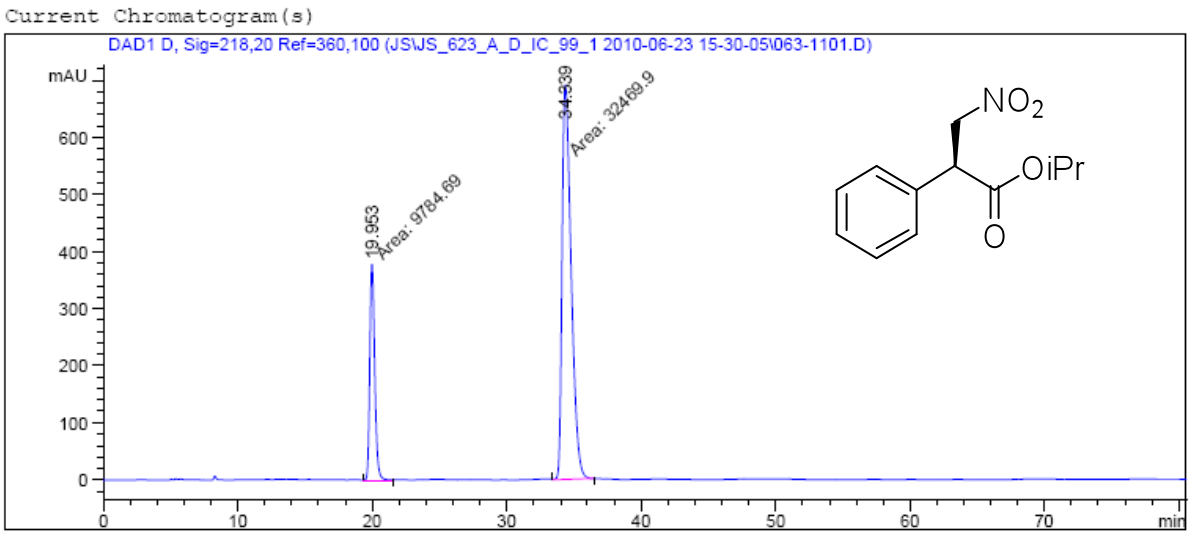
6b


Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_616_617_I_2_IB_99_1_0_6_10C 2010-07-04 10-16-54\072-0101.D)
mAU
NO2
OEt
O
32.590
Area: 37855.4
56.122
Area: 38296.6
min


Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_616_617_I_2_IB_99_1_0_6_10C 2010-07-04 10-16-54\071-0201.D)
mAU
NO2
OEt
O
35.039
Area: 41296.9
59.238
Area: 153509
min

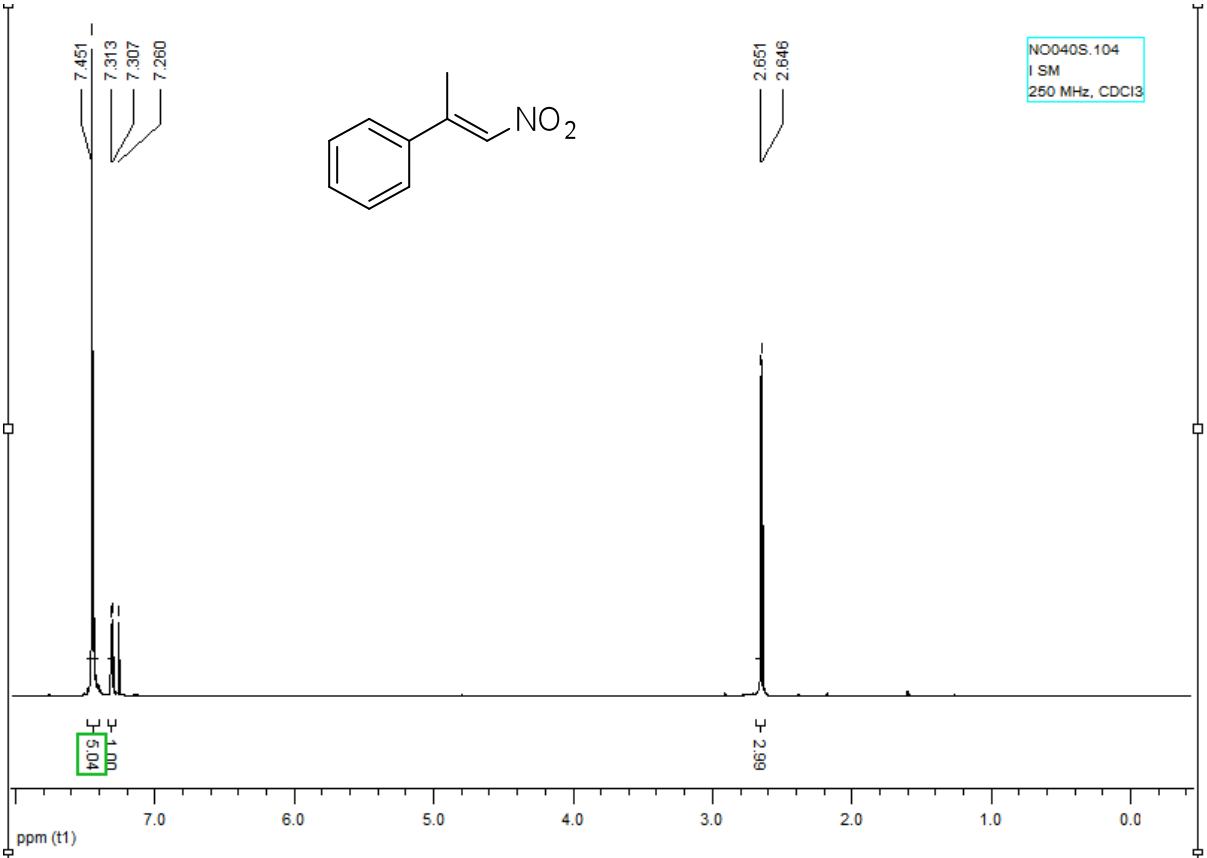
6c

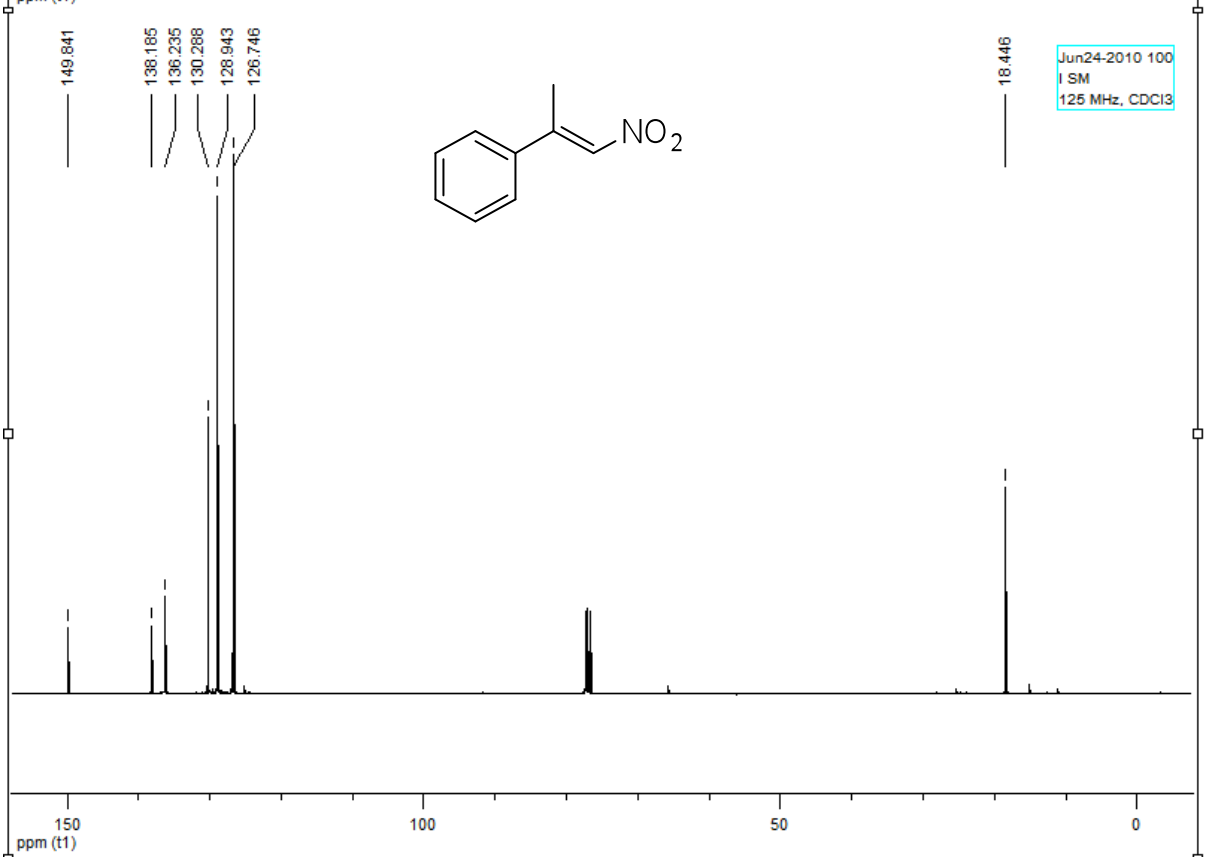

Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_623_A_D_IC_99_1 2010-06-23 15-30-05\062-1001.D)
mAU
19.687
Area: 3025.87
33.801
Area: 3051.35
NO2
OiPr
O
min


Current Chromatogram(s)
DAD1 D, Sig=218,20 Ref=360,100 (JS\JS_623_A_D_IC_99_1 2010-06-23 15-30-05\063-1101.D)
mAU
19.953
Area: 9784.69
34.339
Area: 32469.9
NO2
OiPr
O
min

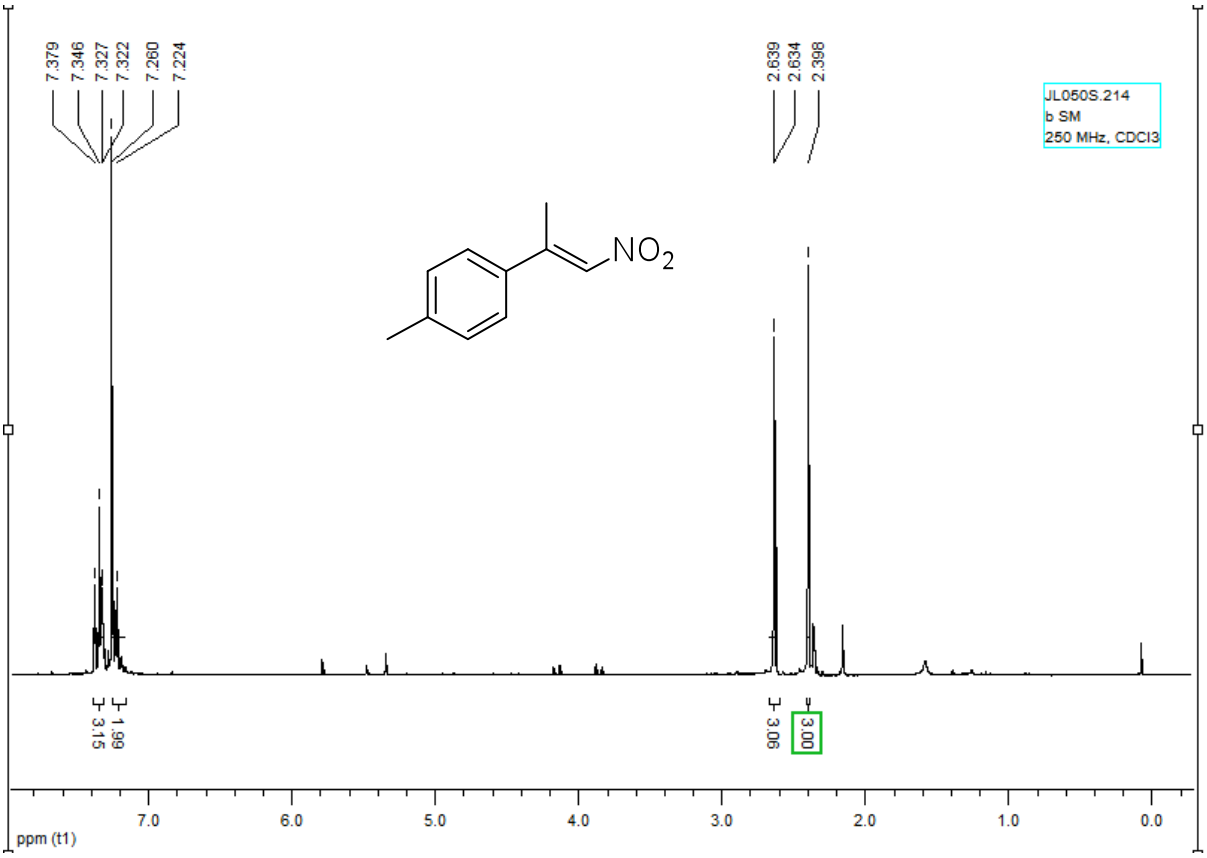
3.3 NMR spectra of the substrates

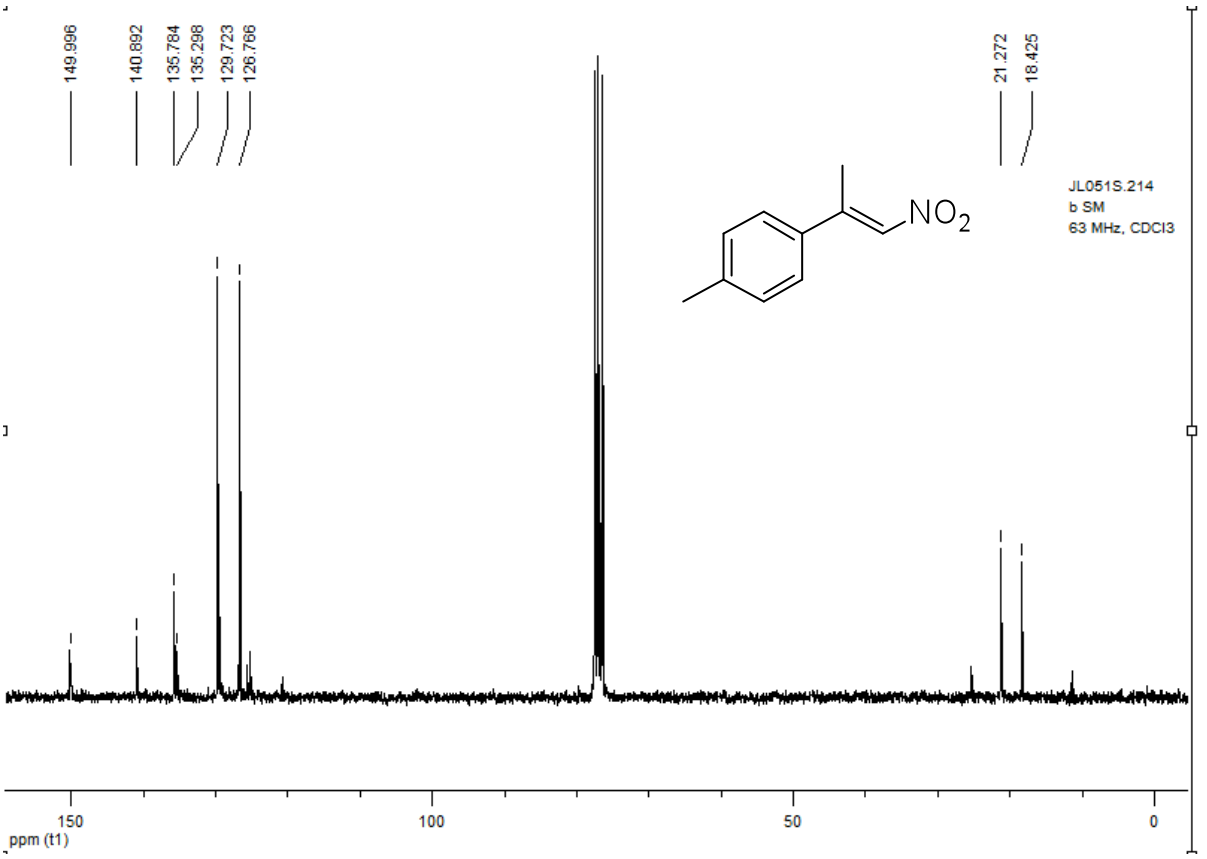
2a



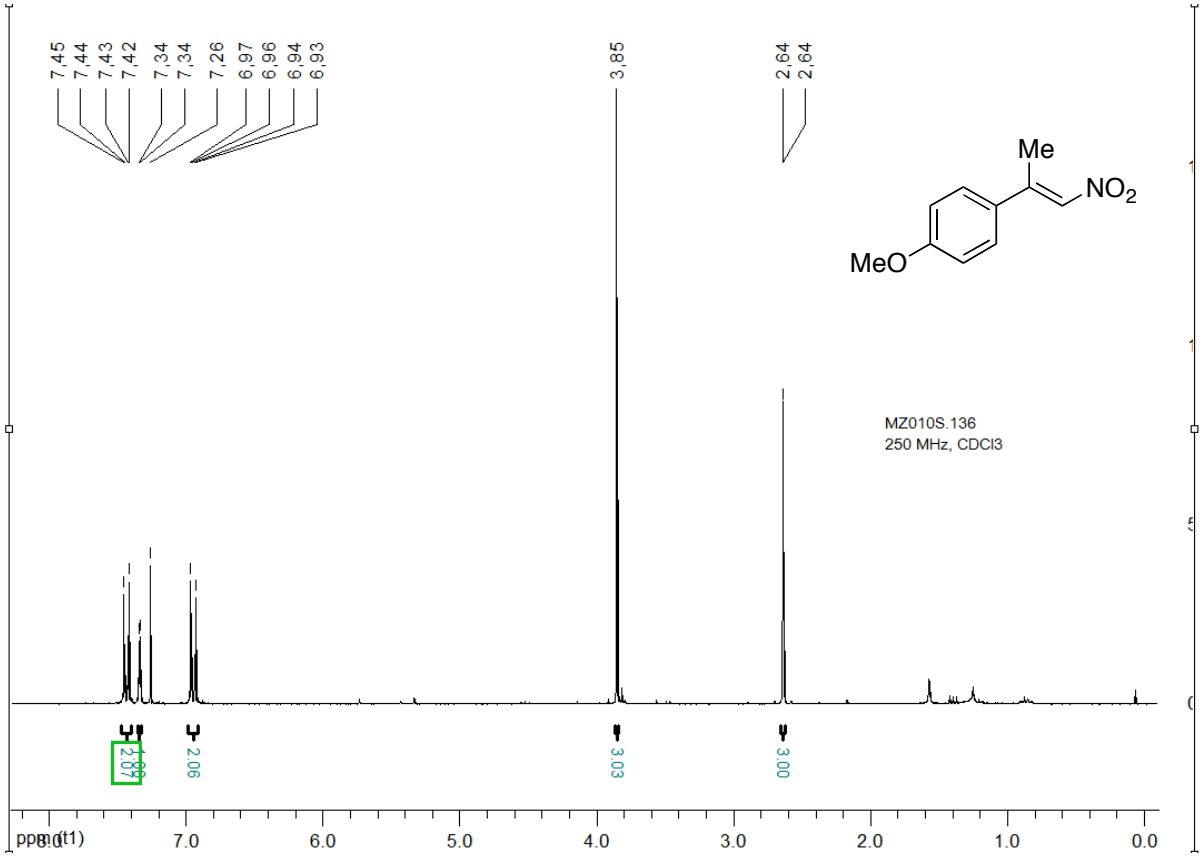


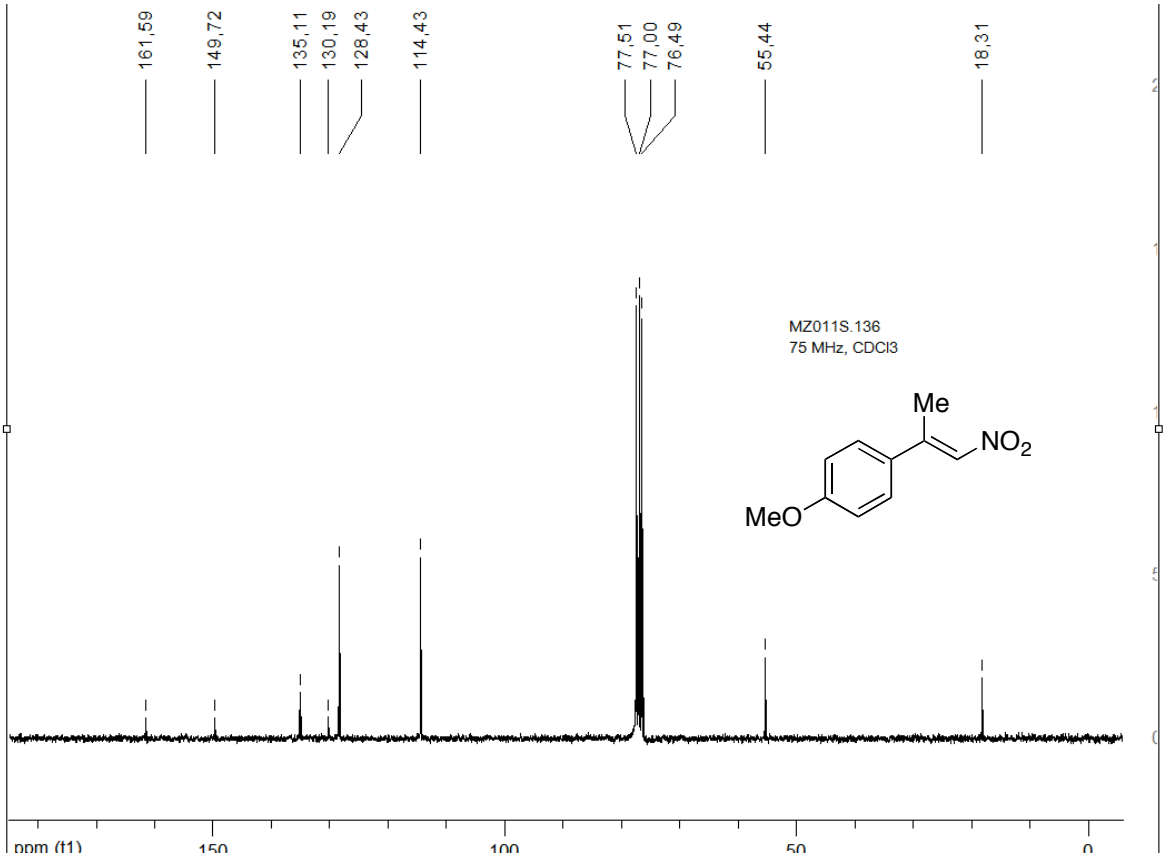
2b


7.379
7.346
7.327
7.322
7.260
7.224
2.639
2.634
2.398
JL050S.214
b SM
250 MHz, CDCl3
NO2
3.15
1.99
3.06
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

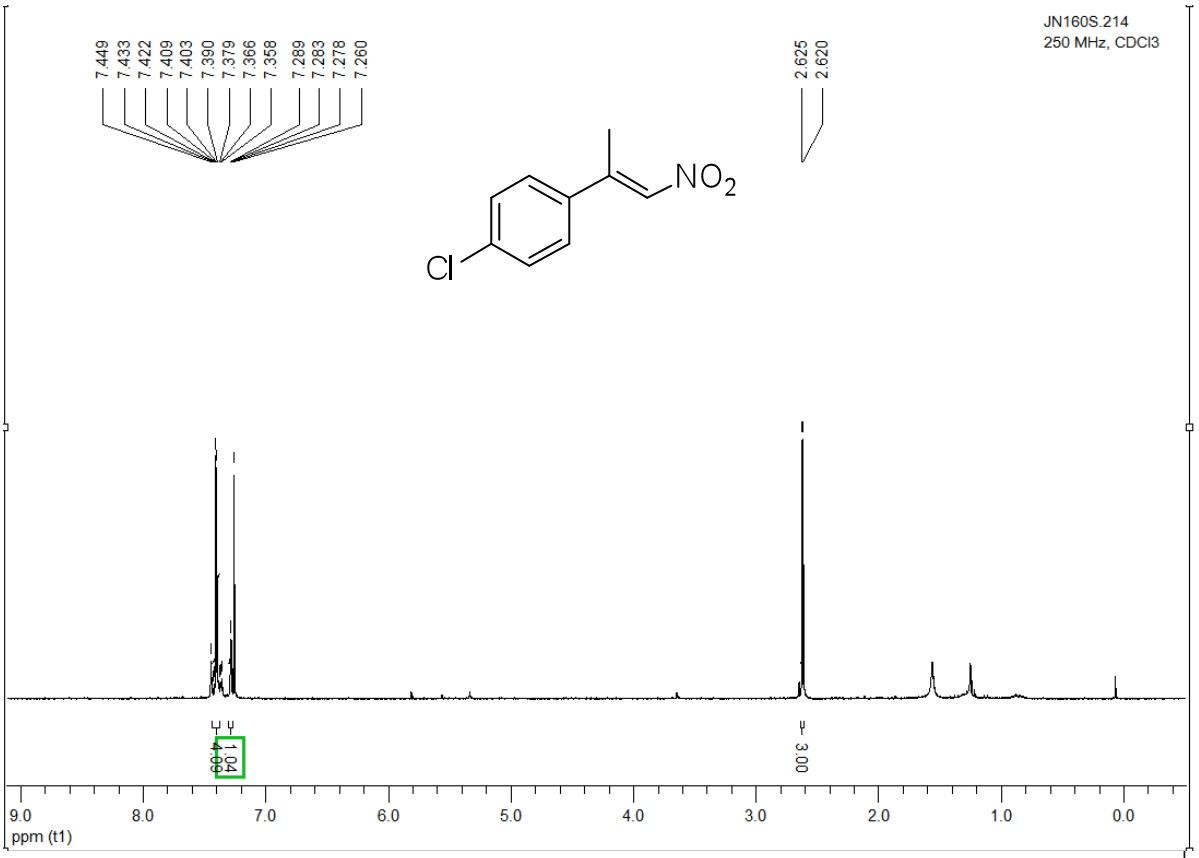

149.996
140.892
135.784
135.298
129.723
126.766
21.272
18.425
JL051S.214
b SM
63 MHz, CDCl3
NO2
150
100
50
0
ppm (t1)

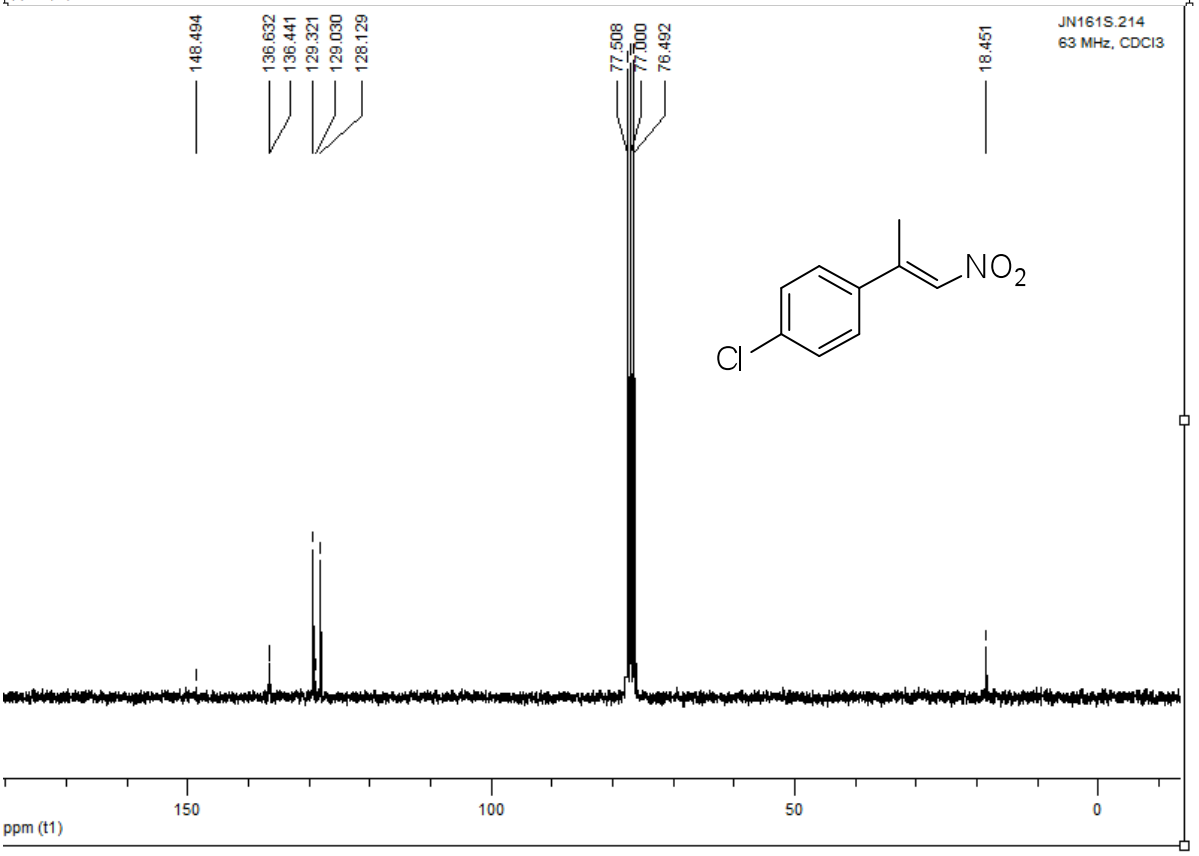
2c


7,45
7,44
7,43
7,42
7,34
7,34
7,26
6,97
6,96
6,94
6,93
3,85
2,64
2,64
Me
NO2
MeO
MZ010S.136
250 MHz, CDCl3
2,07
1,89
2,06
3,03
3,00
ppm (t1)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

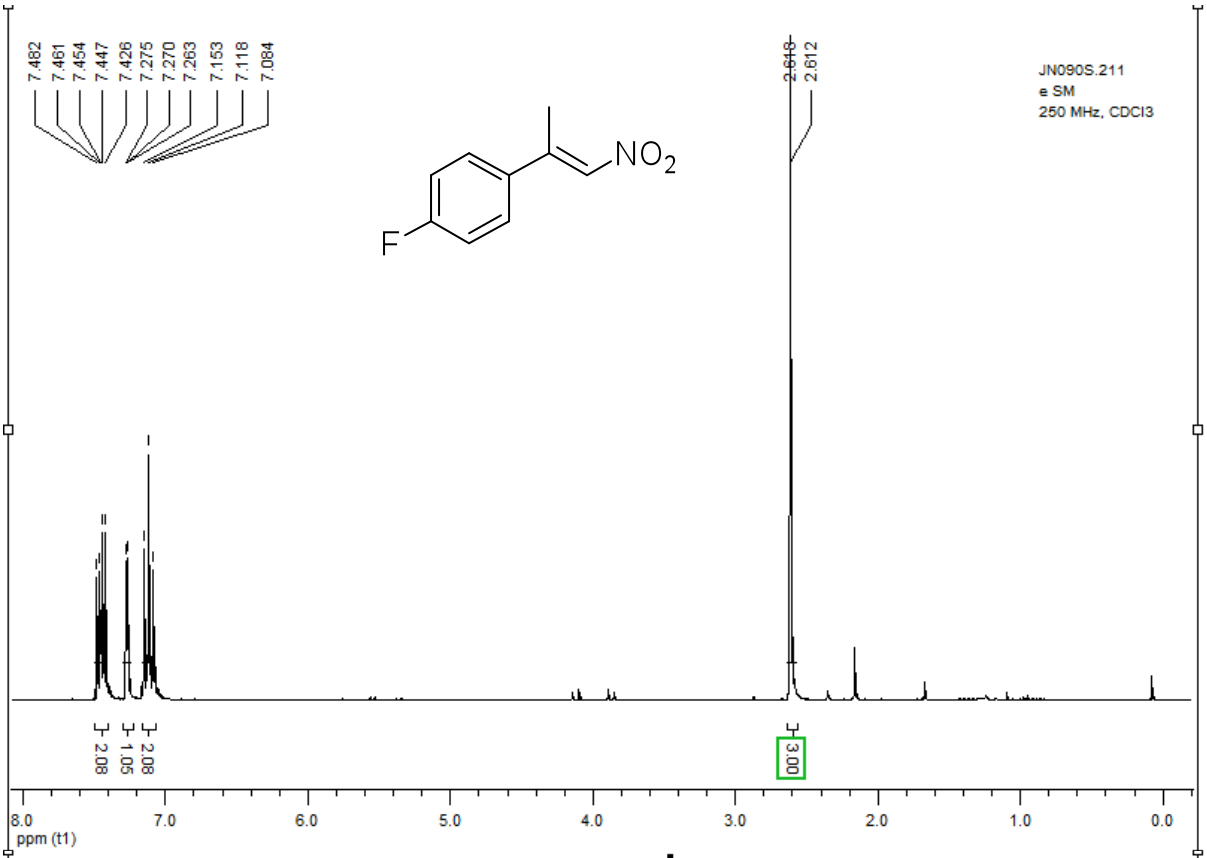

161,59
149,72
135,11
130,19
128,43
114,43
77,51
77,00
76,49
55,44
18,31
MZ011S.136
75 MHz, CDCl3
Me
NO2
MeO
ppm (t1)
150
100
50
0

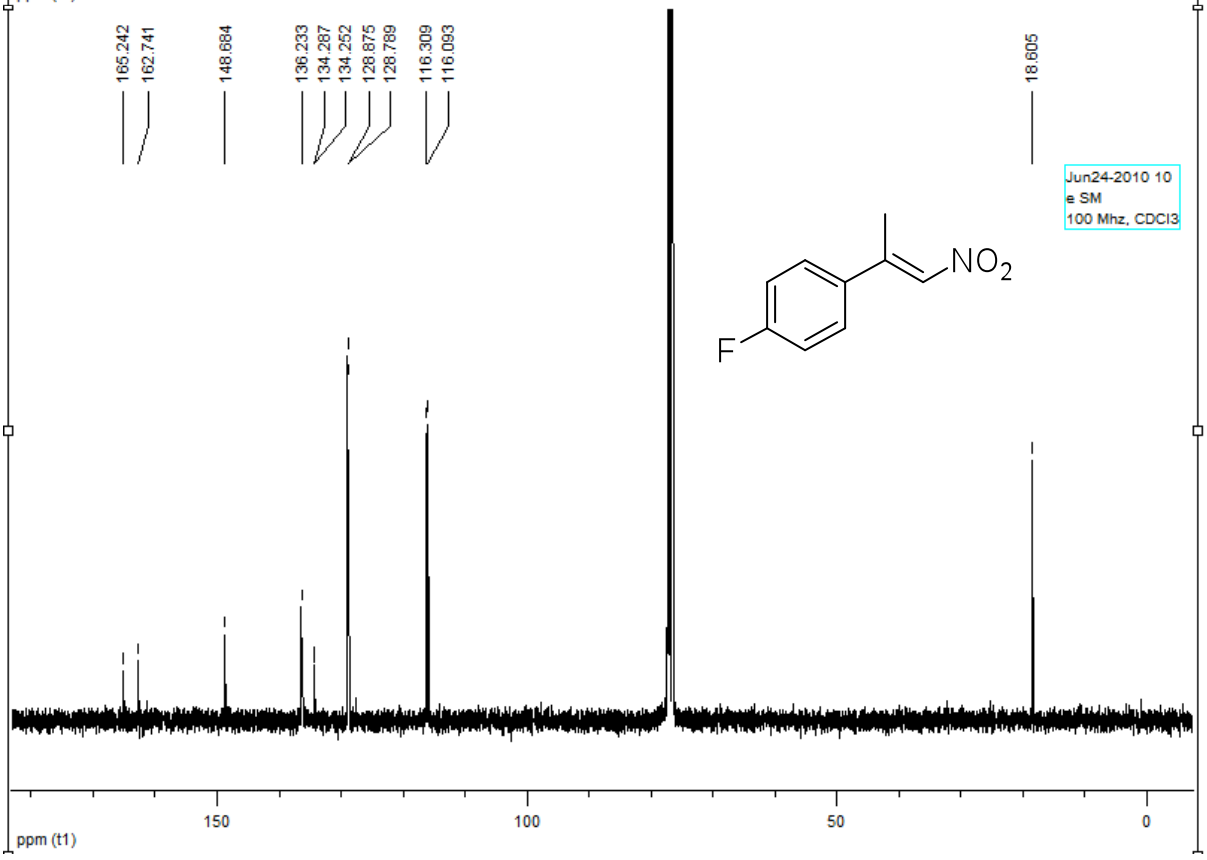
2d


JN160S.214
250 MHz, CDCl3
7.449
7.433
7.422
7.409
7.403
7.390
7.379
7.366
7.358
7.289
7.283
7.278
7.260
2.625
2.620
NO2
Cl
4.09
1.04
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

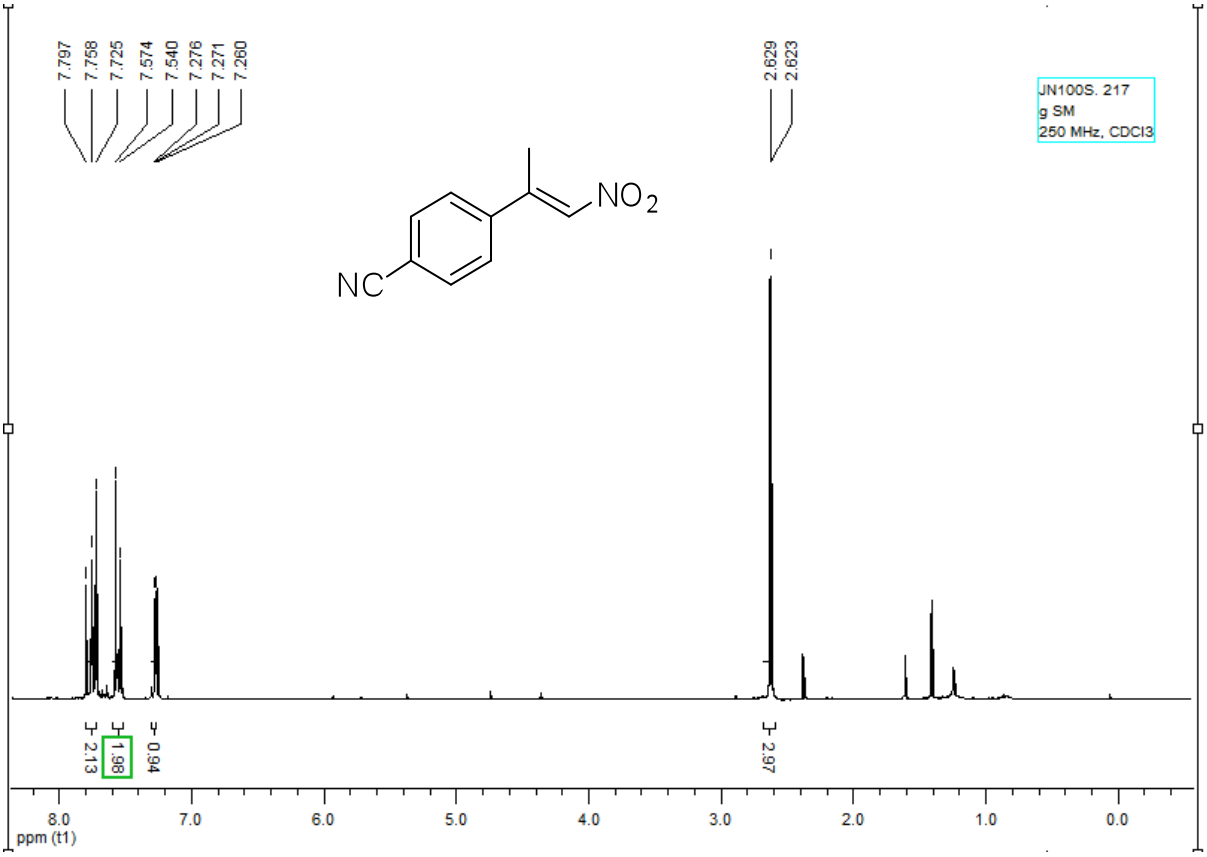

JN161S.214
63 MHz, CDCl3
148.494
136.632
136.441
129.321
129.030
128.129
77.508
77.000
76.492
18.451
NO2
Cl
150
100
50
0
ppm (t1)

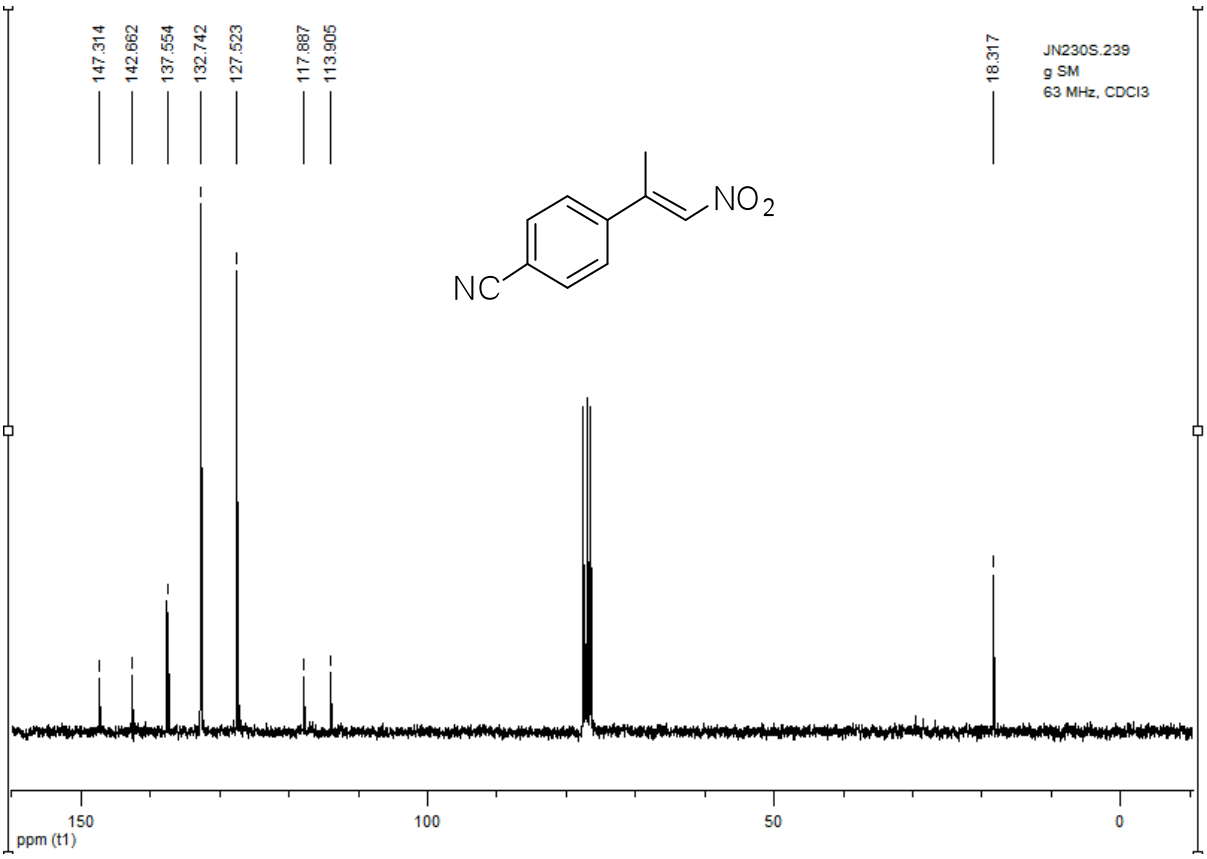
2e


7.482
7.461
7.454
7.447
7.426
7.275
7.270
7.263
7.153
7.118
7.084
2.618
2.612
JN090S.211
e SM
250 MHz, CDCl3
NO2
F
2.08
1.05
2.08
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

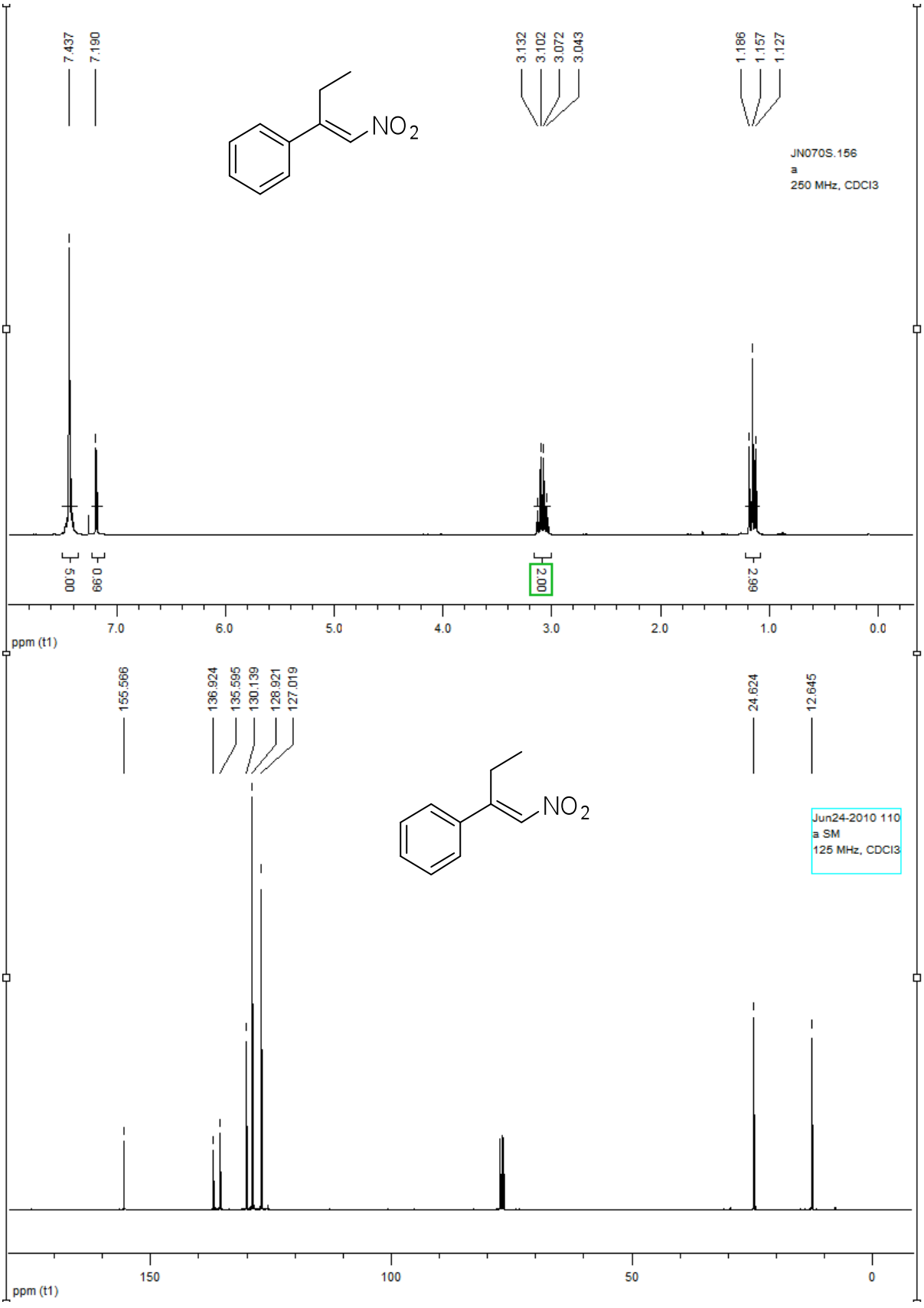

165.242
162.741
148.684
136.233
134.287
134.252
128.875
128.789
116.309
116.093
18.605
Jun24-2010 10
e SM
100 Mhz, CDCl3
NO2
F
150
100
50
0
ppm (t1)

2f

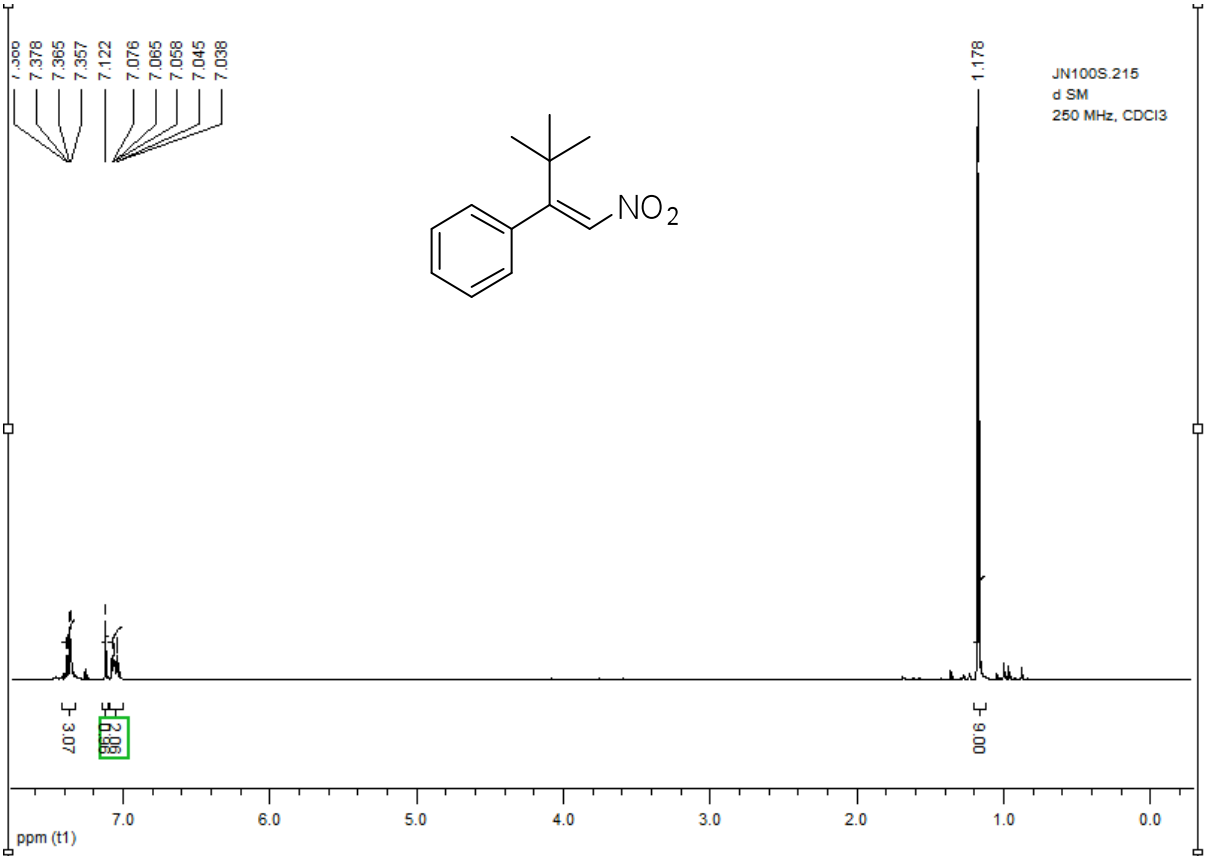

7.797
7.758
7.725
7.574
7.540
7.276
7.271
7.260
2.629
2.623
JN100S. 217
g SM
250 MHz, CDCl3
NO2
NC
2.13
1.98
0.94
2.37
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

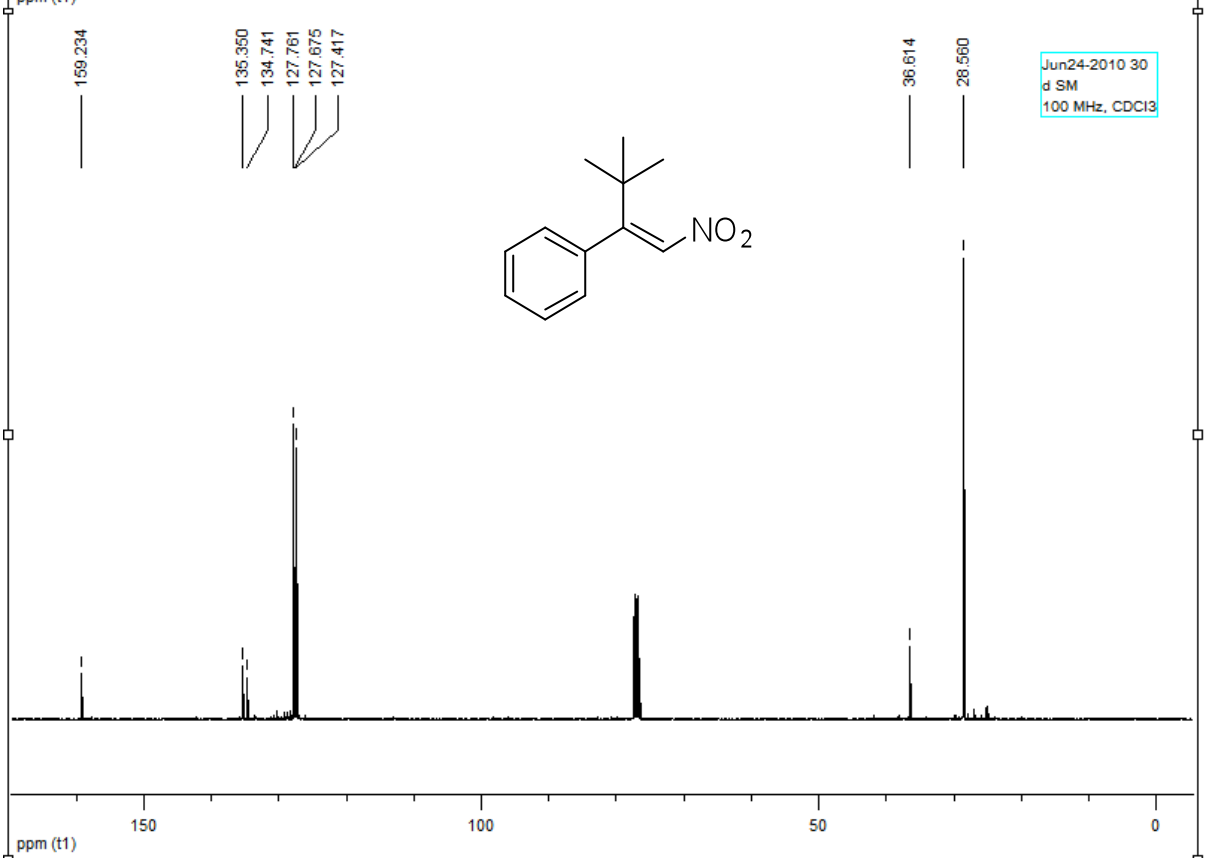

147.314
142.662
137.554
132.742
127.523
117.887
113.905
18.317
JN230S.239
g SM
63 MHz, CDCl3
NO2
NC
150
100
50
0
ppm (t1)

2g

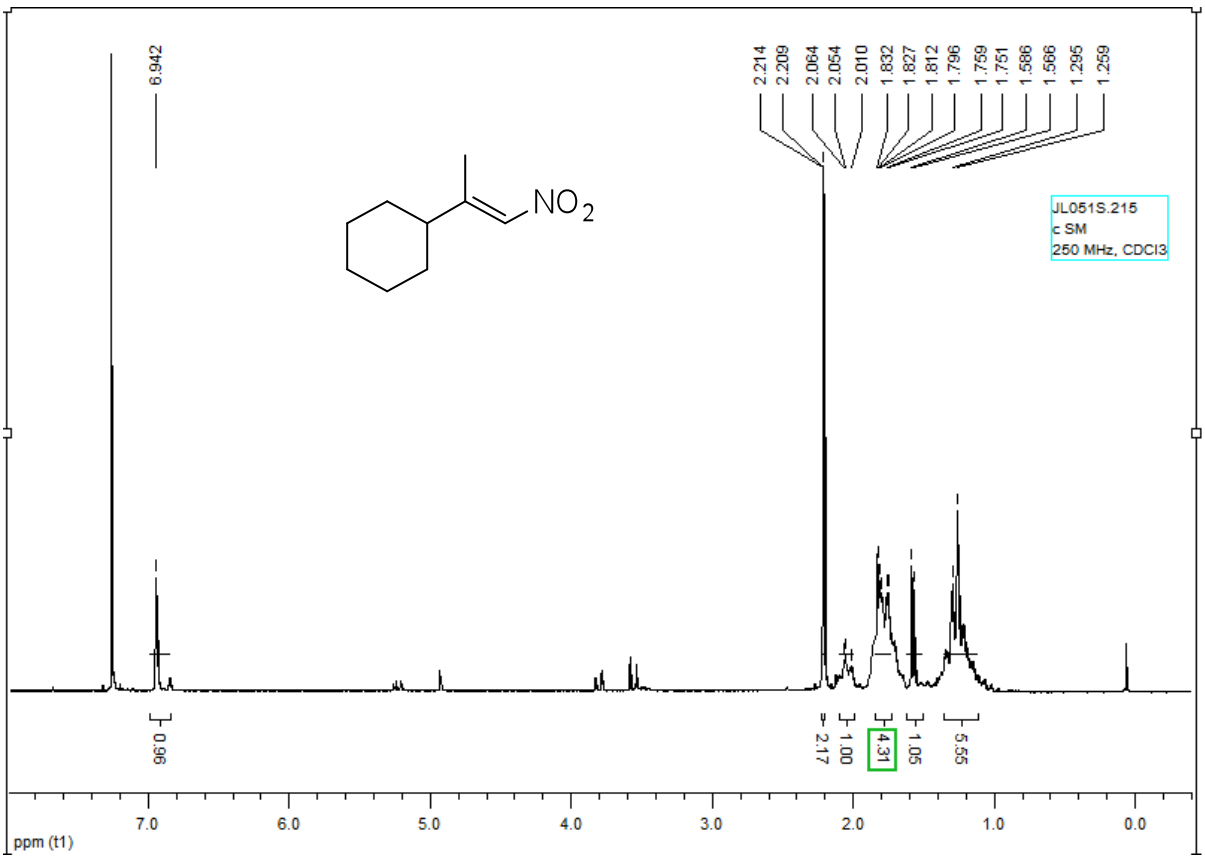

7.437
7.190
3.132
3.102
3.072
3.043
1.186
1.157
1.127
NO2
JN070S.156
a
250 MHz, CDCl3
5.00
0.99
2.00
2.99
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
155.566
136.924
135.595
130.139
128.921
127.019
24.624
12.645
NO2
Jun24-2010 110
a SM
125 MHz, CDCl3
150
100
50
0
ppm (t1)

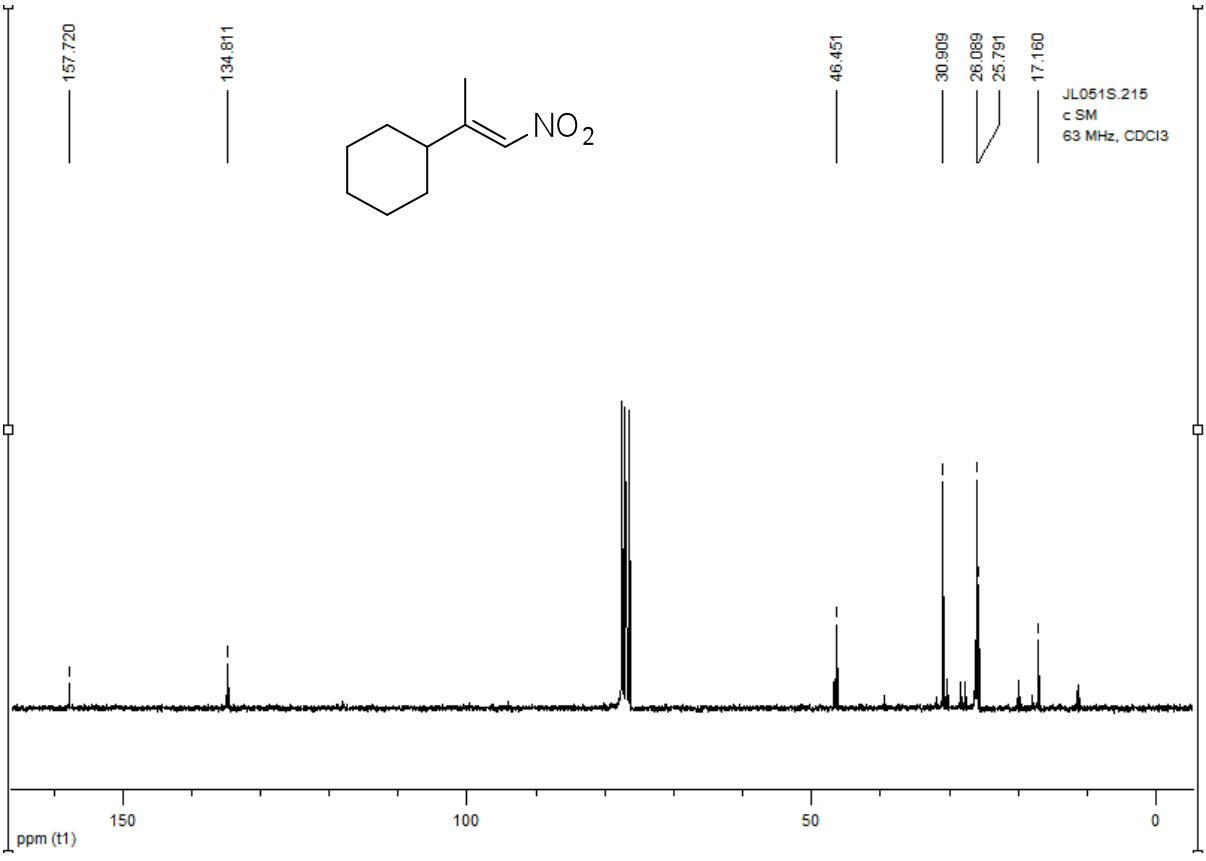
2h


7.378
7.365
7.357
7.122
7.076
7.065
7.058
7.045
7.038
1.178
JN100S.215
d SM
250 MHz, CDCl3
NO2
3.07
2.08
9.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

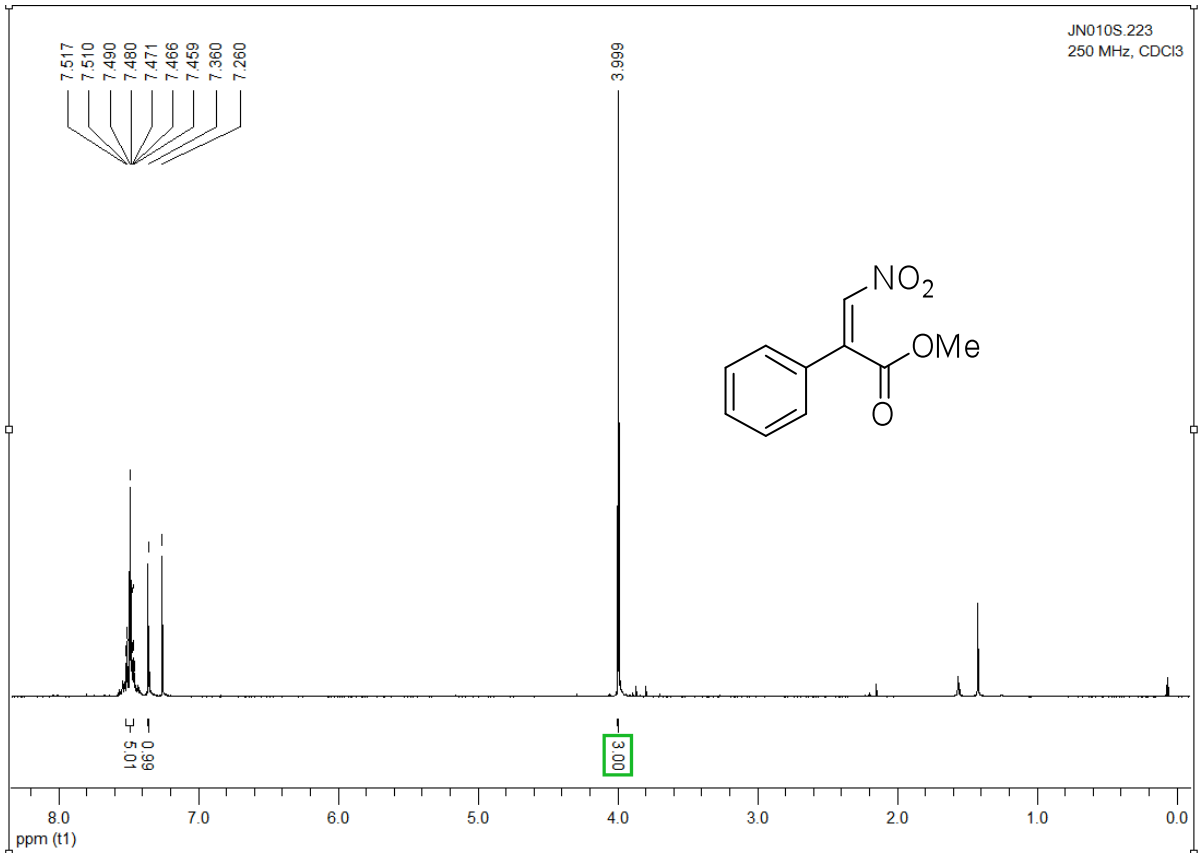

159.234
135.350
134.741
127.761
127.675
127.417
36.614
28.560
Jun24-2010 30
d SM
100 MHz, CDCl3
NO2
150
100
50
0
ppm (t1)

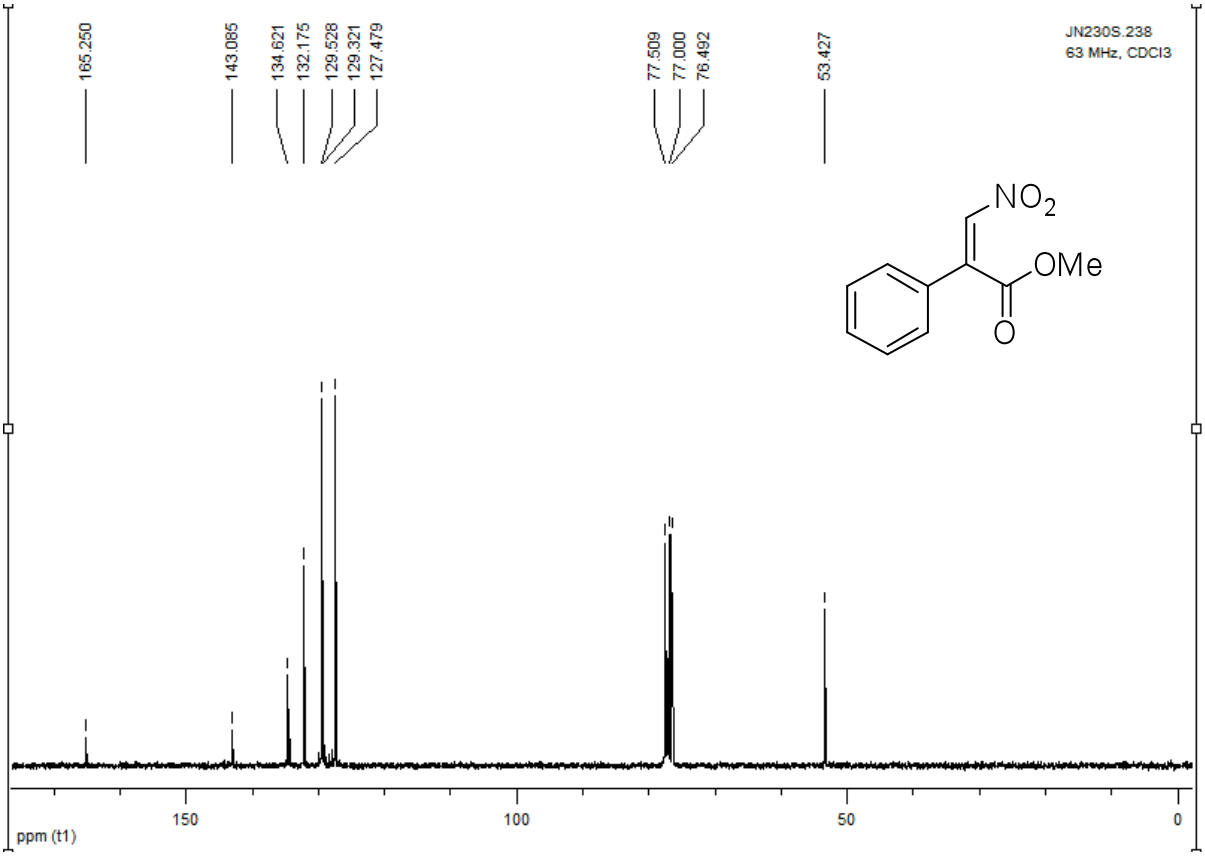
2i


6.942
2.214
2.209
2.064
2.054
2.010
1.832
1.827
1.812
1.796
1.759
1.751
1.586
1.566
1.295
1.259
NO2
JL051S.215
c SM
250 MHz, CDCl3
0.96
2.17
1.00
1.31
1.05
5.55
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

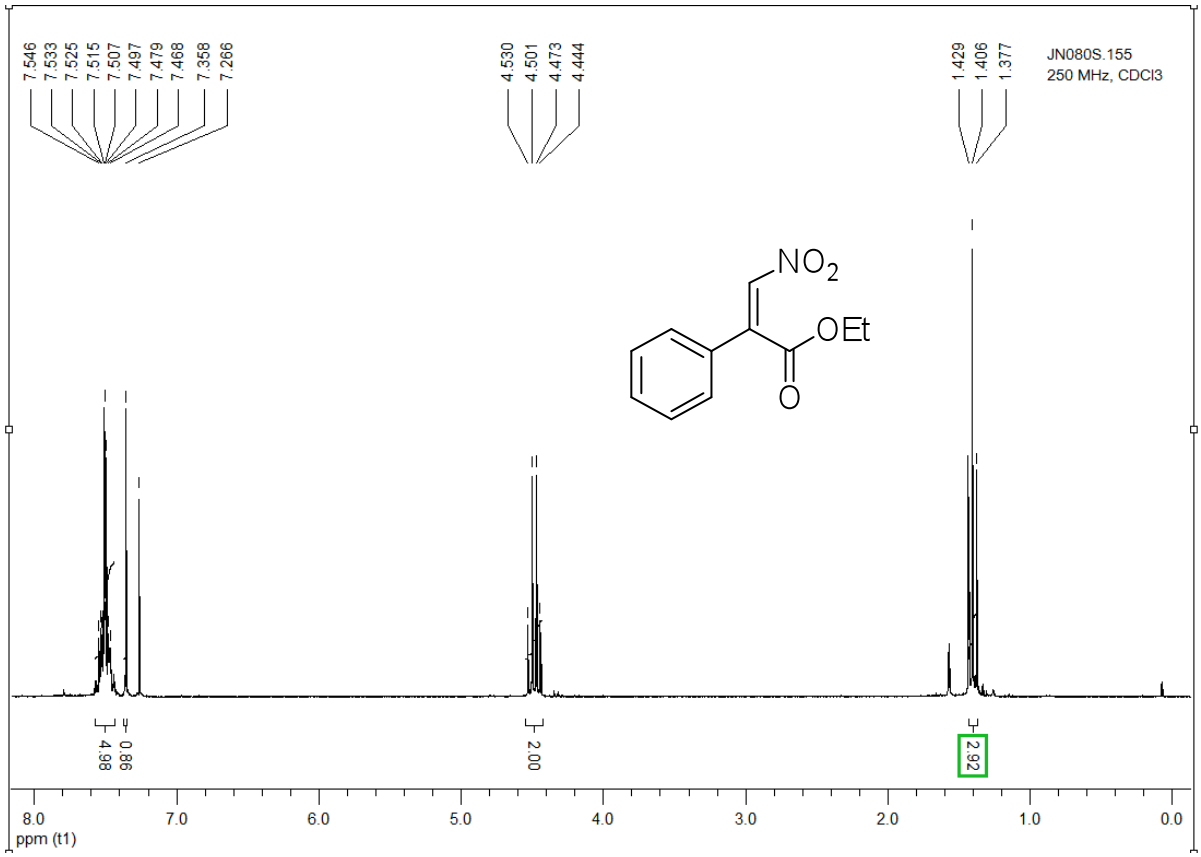

157.720
134.811
46.451
30.909
26.089
25.791
17.160
NO2
JL051S.215
c SM
63 MHz, CDCl3
150
100
50
0
ppm (t1)

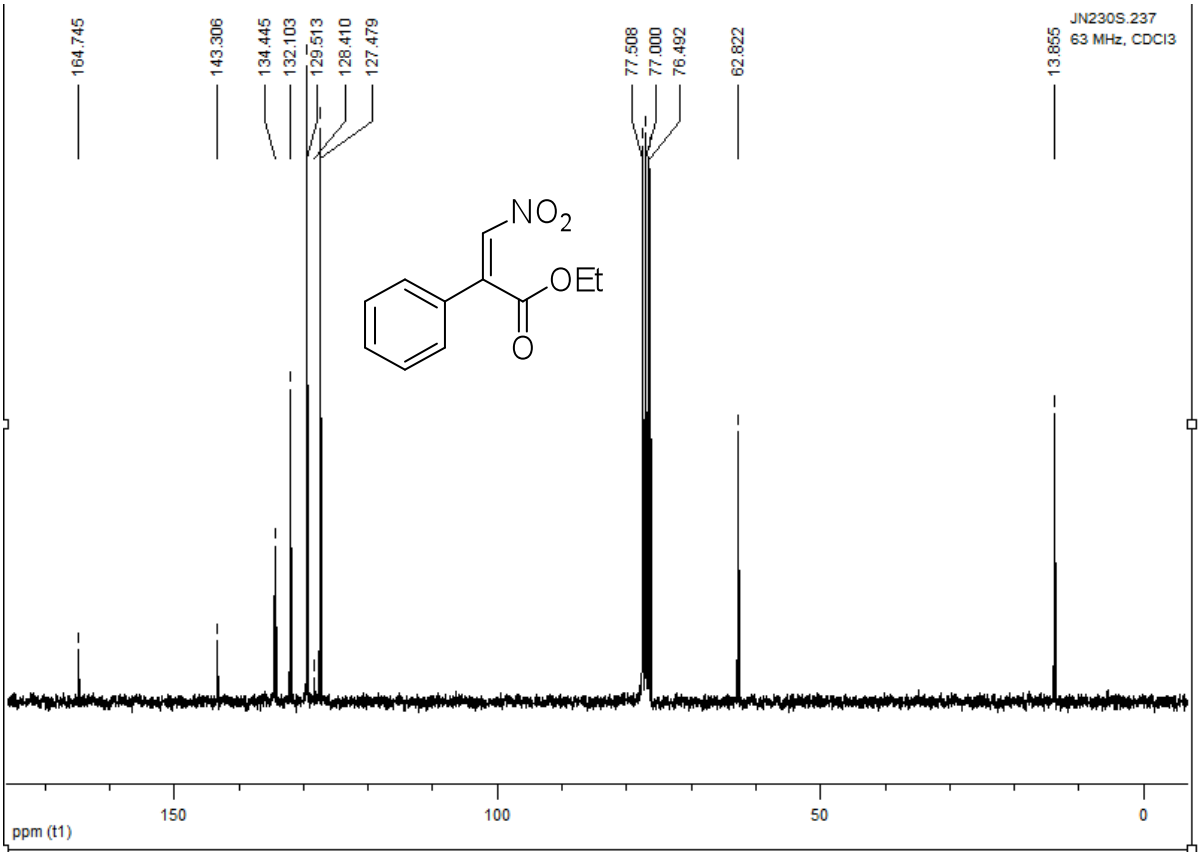
5a


JN010S.223
250 MHz, CDCl3
7.517
7.510
7.490
7.480
7.471
7.466
7.459
7.360
7.260
3.999
NO2
OMe
O
6.01
0.99
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

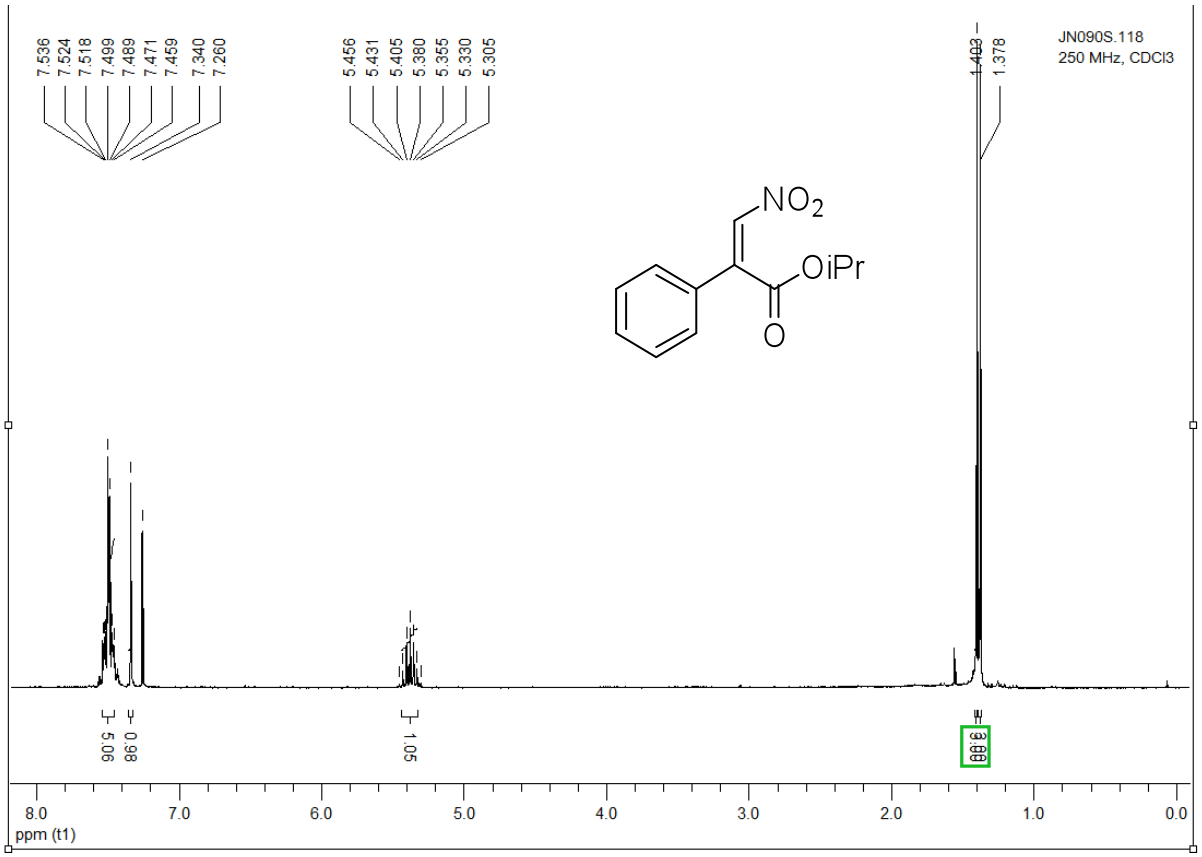

JN230S.238
63 MHz, CDCl3
165.250
143.085
134.621
132.175
129.528
129.321
127.479
77.509
77.000
76.492
53.427
NO2
OMe
O
150
100
50
0
ppm (t1)

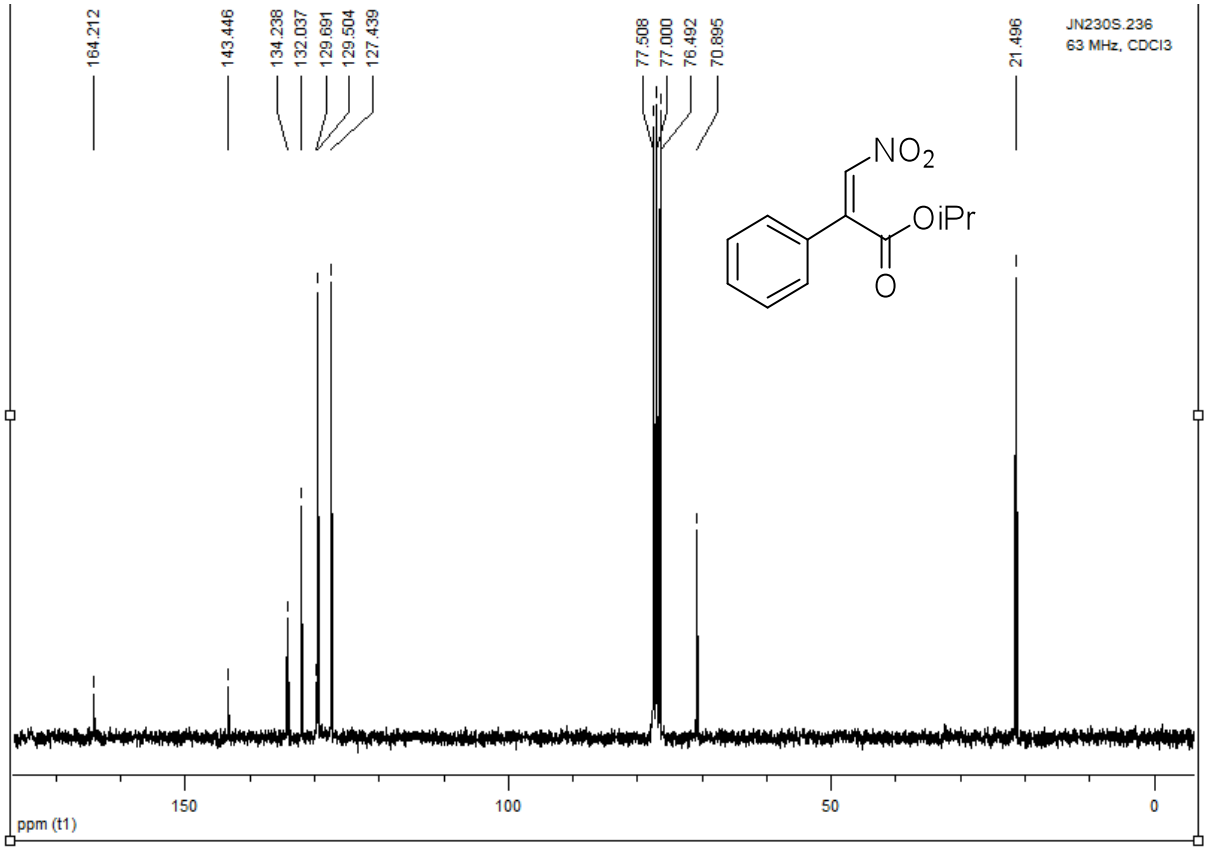
5b


7.546
7.533
7.525
7.515
7.507
7.497
7.479
7.468
7.358
7.266
4.530
4.501
4.473
4.444
1.429
1.406
1.377
JN080S.155
250 MHz, CDCl3
NO2
OEt
O
4.98
0.98
2.00
2.92
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


164.745
143.306
134.445
132.103
129.513
128.410
127.479
77.508
77.000
76.492
62.822
13.855
JN230S.237
63 MHz, CDCl3
NO2
OEt
O
150
100
50
0
ppm (t1)

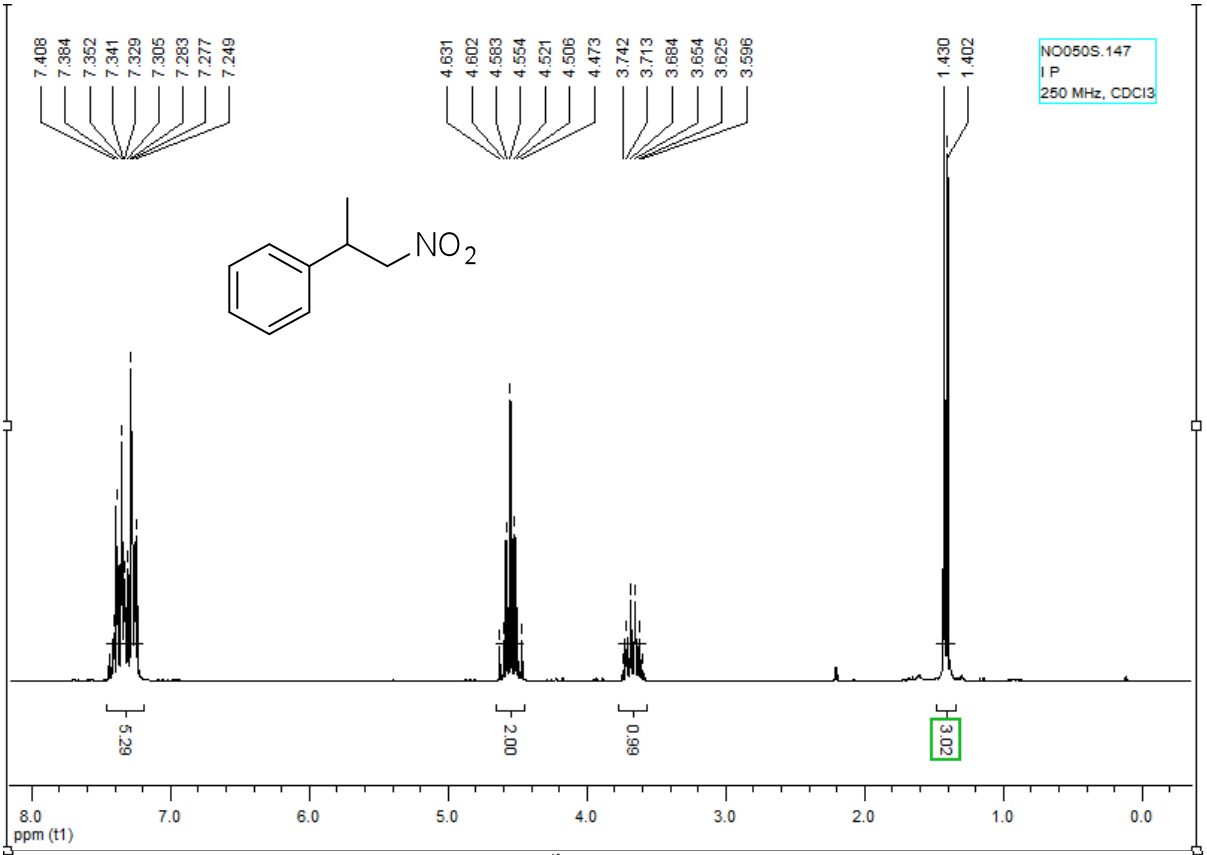
5c

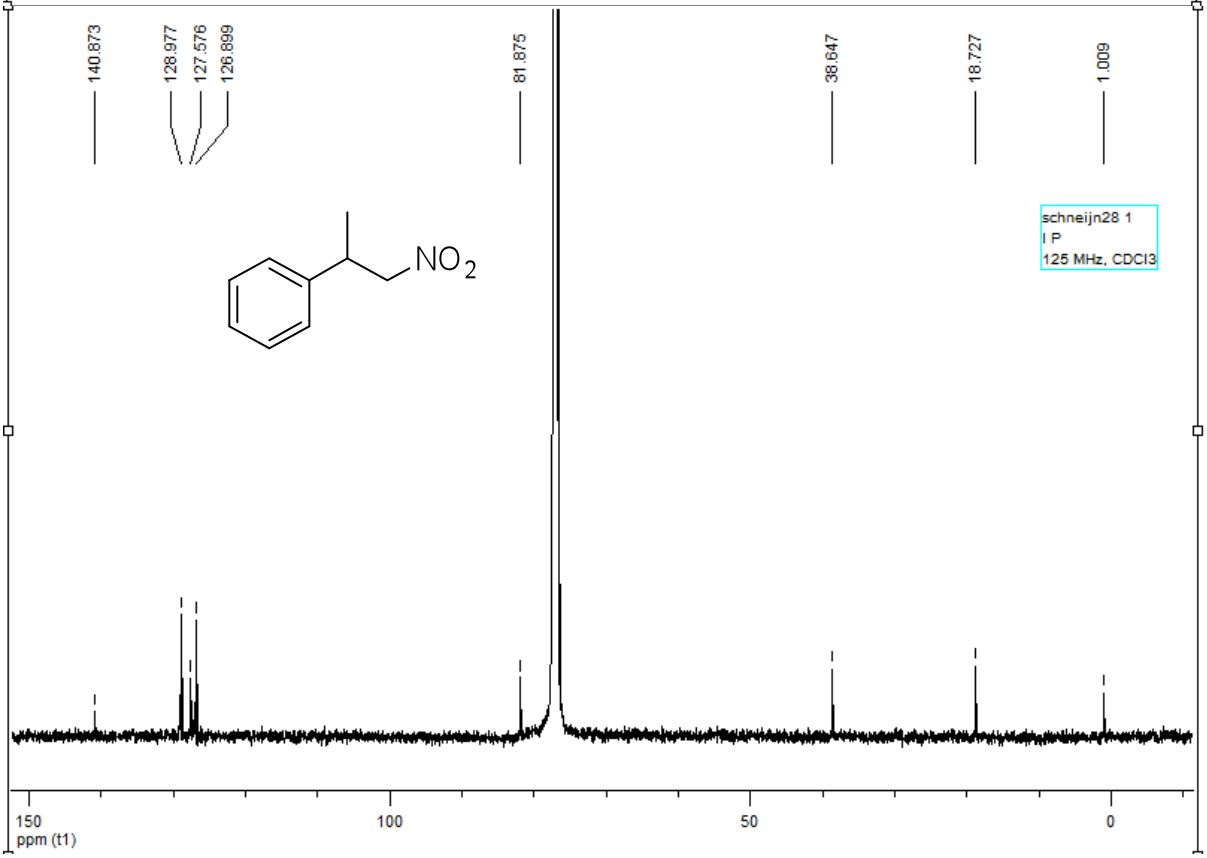

7.536
7.524
7.518
7.499
7.489
7.471
7.459
7.340
7.260
5.456
5.431
5.405
5.380
5.355
5.330
5.305
1.403
1.378
JN090S.118
250 MHz, CDCl3
NO2
OiPr
O
5.06
0.98
1.06
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


164.212
143.446
134.238
132.037
129.691
129.504
127.439
77.508
77.000
76.492
70.895
21.496
JN230S.236
63 MHz, CDCl3
NO2
OiPr
O
150
100
50
0
ppm (t1)

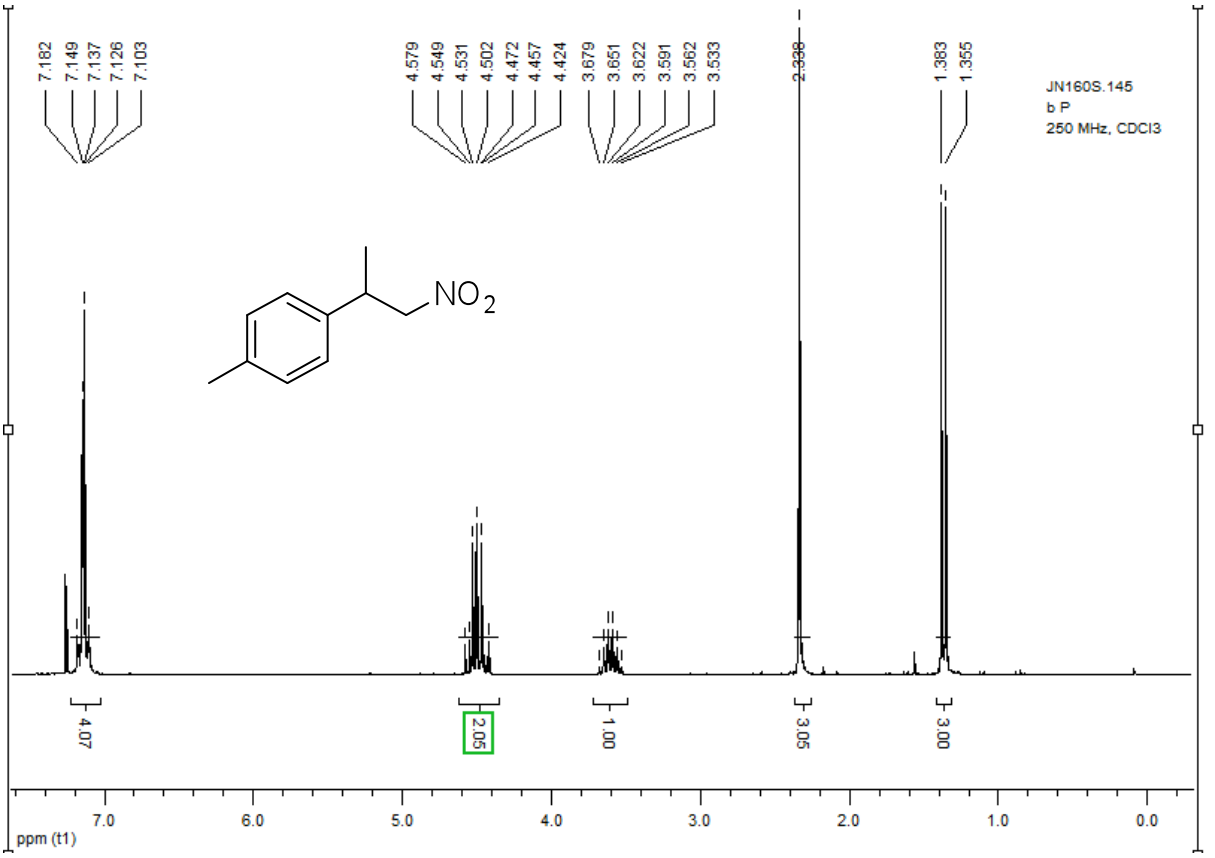
NMR spectra of hydrogenated compounds

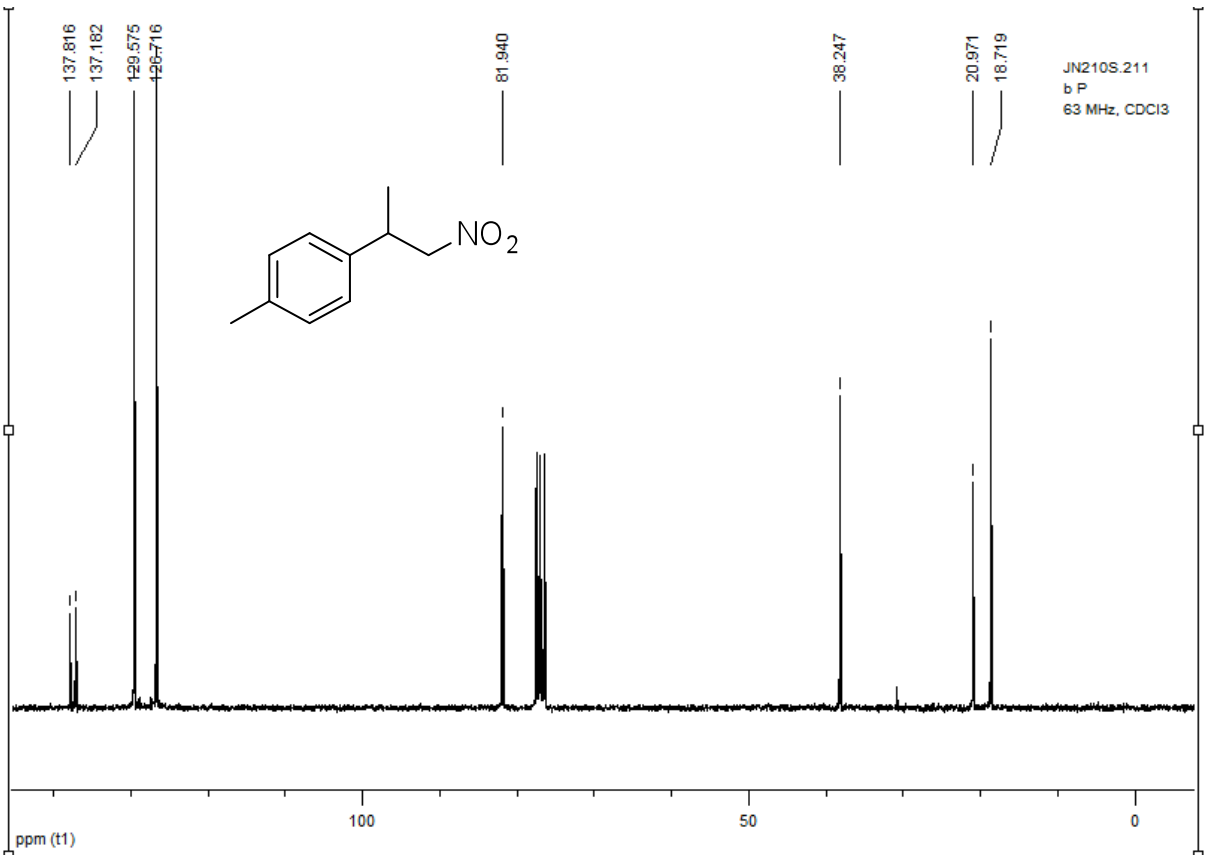
4a



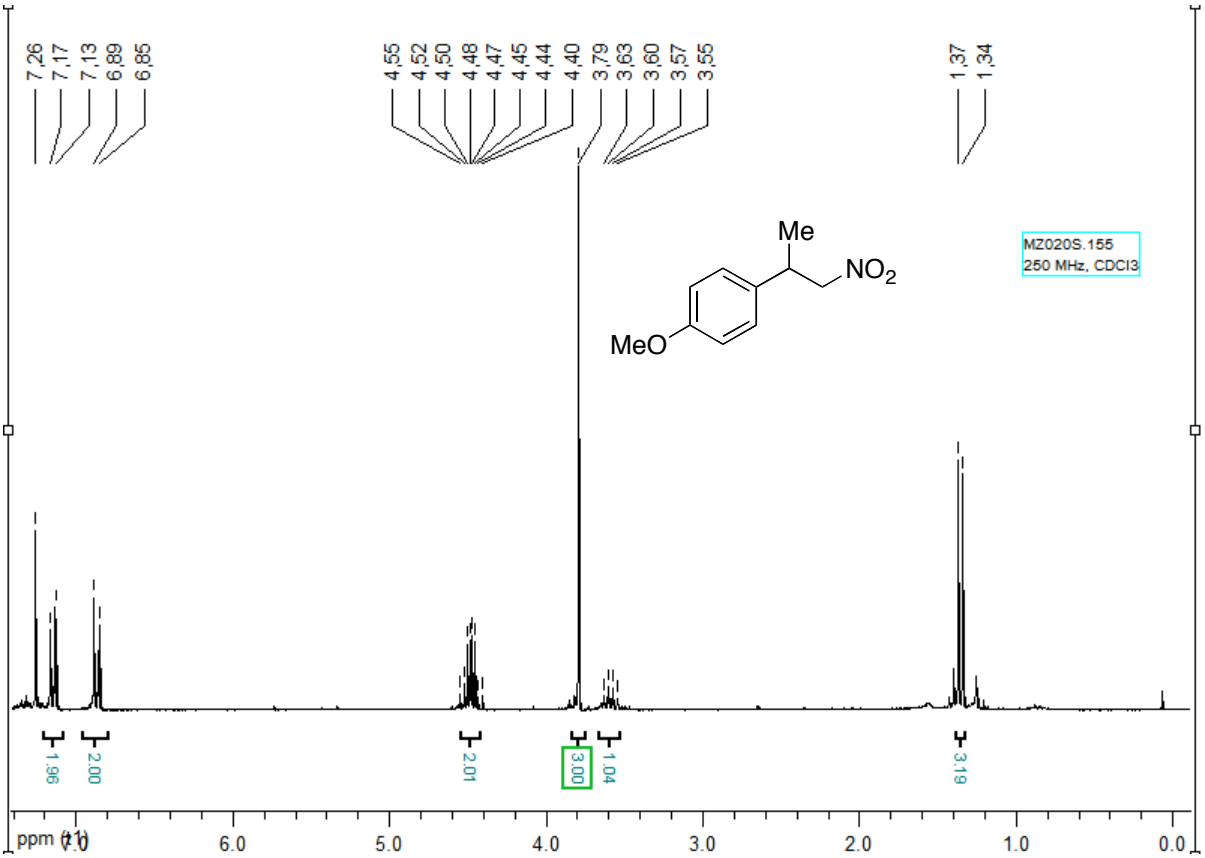


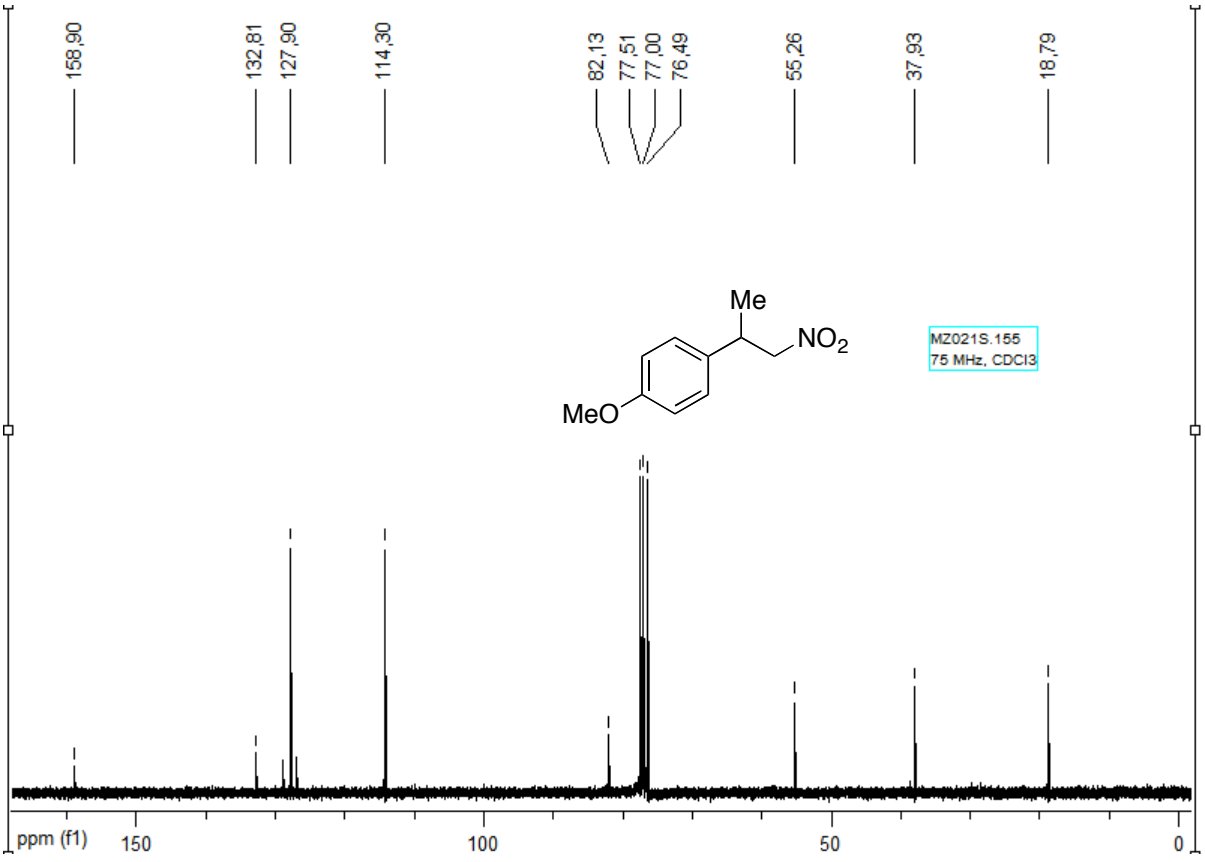
4b


7.182
7.149
7.137
7.126
7.103
4.579
4.549
4.531
4.502
4.472
4.457
4.424
3.679
3.651
3.622
3.591
3.562
3.533
2.398
1.383
1.355
JN160S.145
b P
250 MHz, CDCl3
NO2
4.07
2.05
1.00
3.06
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

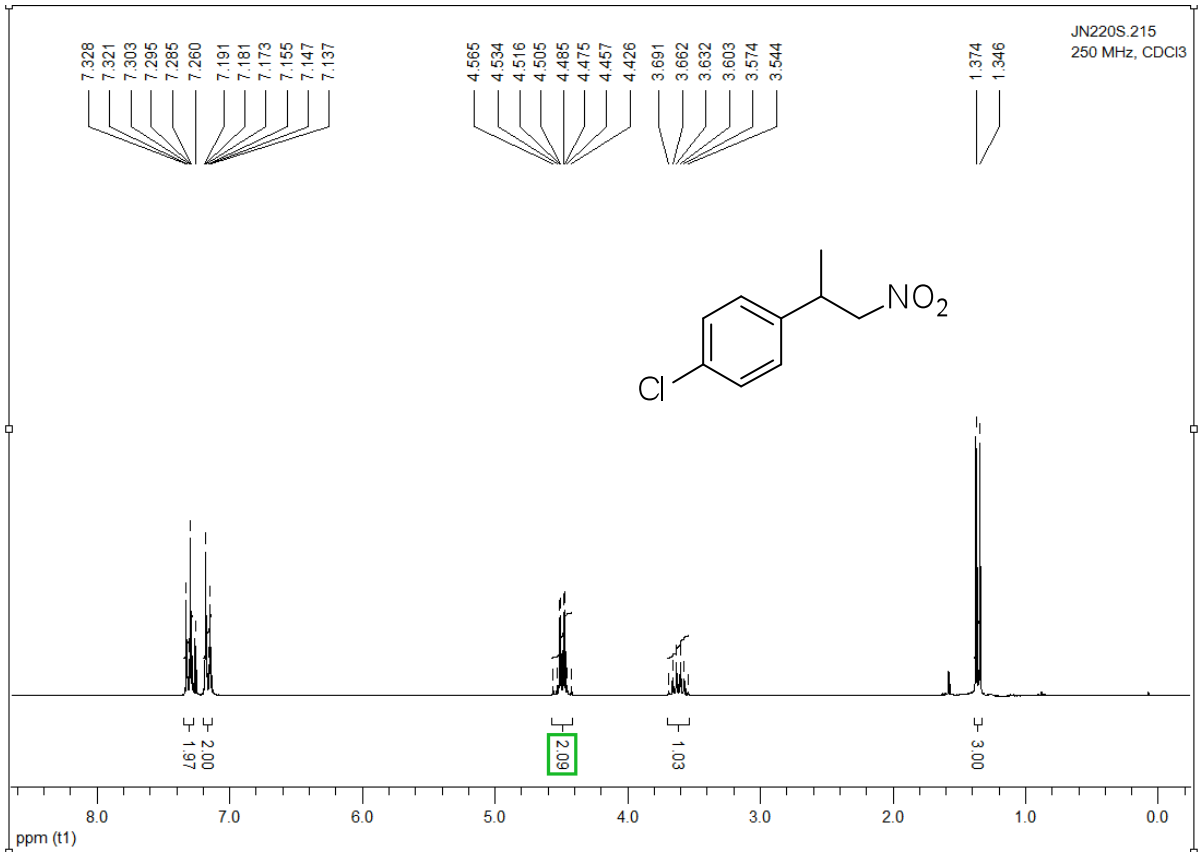

137.816
137.182
129.575
126.716
81.940
38.247
20.971
18.719
JN210S.211
b P
63 MHz, CDCl3
NO2
100
50
0
ppm (t1)

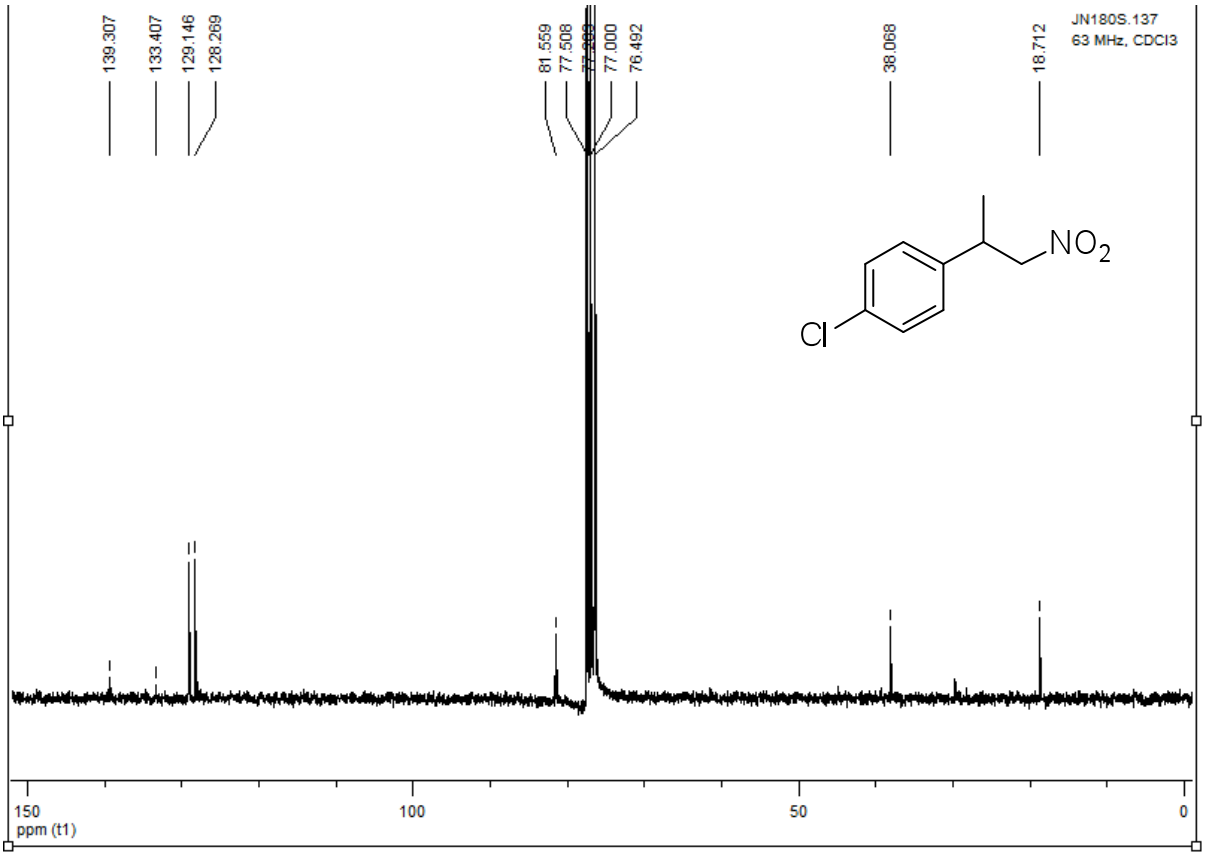
4c


7,26
7,17
7,13
6,89
6,85
4,55
4,52
4,50
4,48
4,47
4,45
4,44
4,40
3,79
3,63
3,60
3,57
3,55
1,37
1,34
Me
NO2
MeO
MZ020S.155
250 MHz, CDCl3
1.96
2.00
2.01
3.00
1.04
3.19
ppm (f1)
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

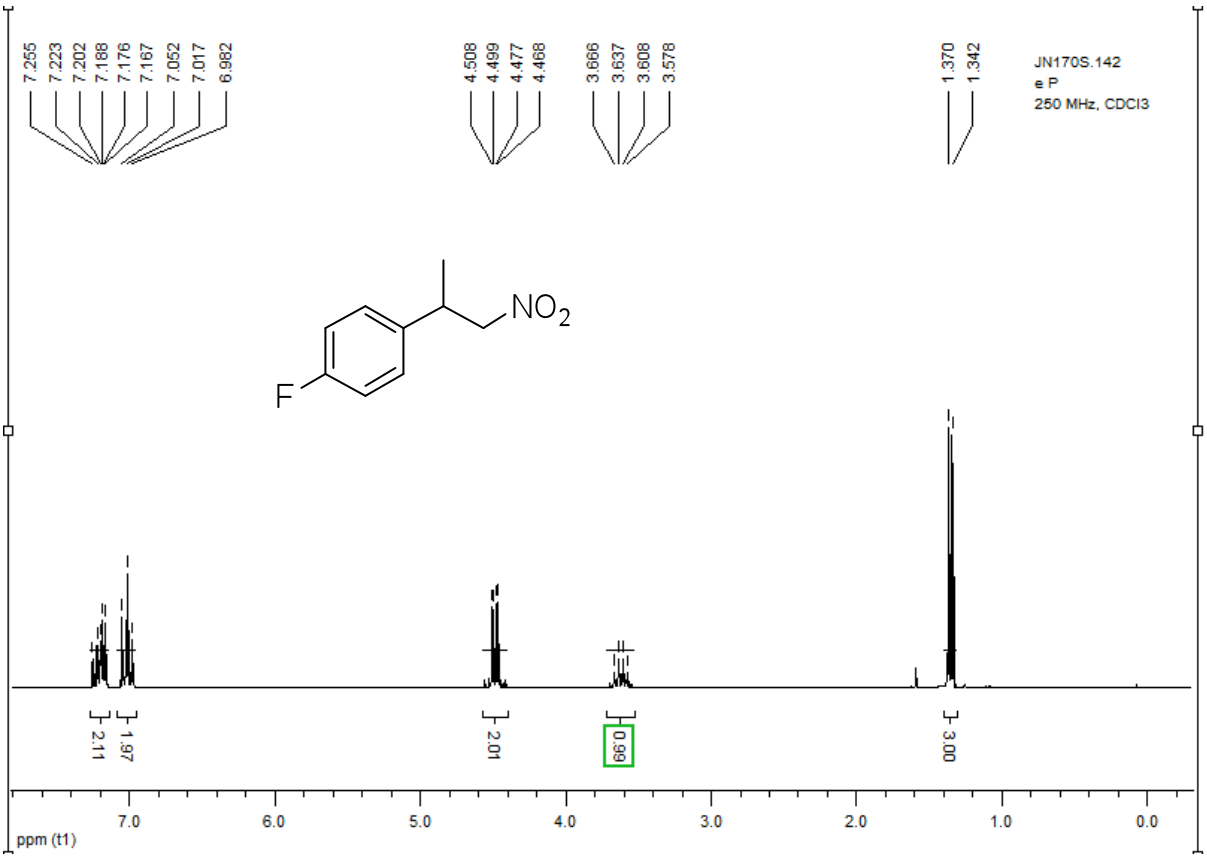

158,90
132,81
127,90
114,30
82,13
77,51
77,00
76,49
55,26
37,93
18,79
Me
NO2
MeO
MZ021S.155
75 MHz, CDCl3
ppm (f1)
150
100
50
0

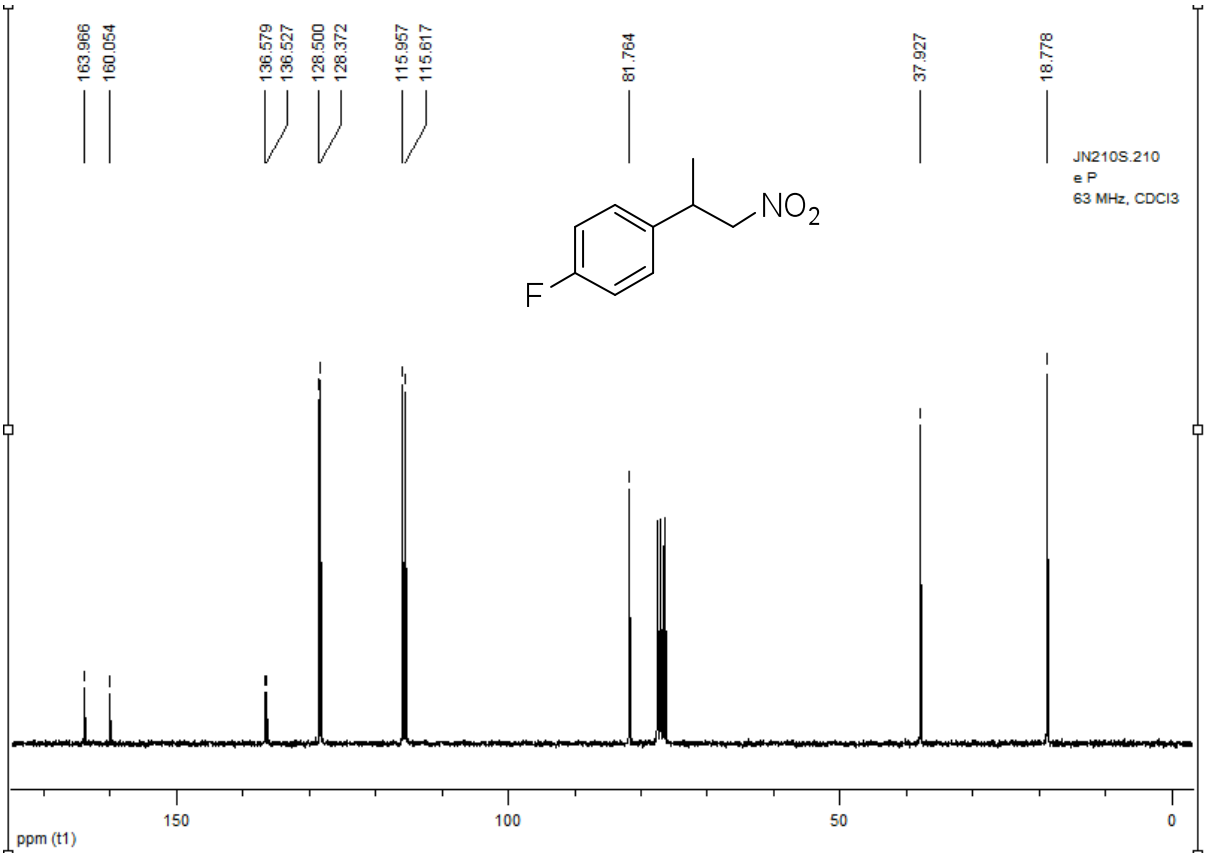
4d


JN220S.215
250 MHz, CDCl3
7.328
7.321
7.303
7.295
7.285
7.260
7.191
7.181
7.173
7.155
7.147
7.137
4.565
4.534
4.516
4.505
4.485
4.475
4.457
4.426
3.691
3.662
3.632
3.603
3.574
3.544
1.374
1.346
NO2
Cl
1.97
2.00
2.09
1.03
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

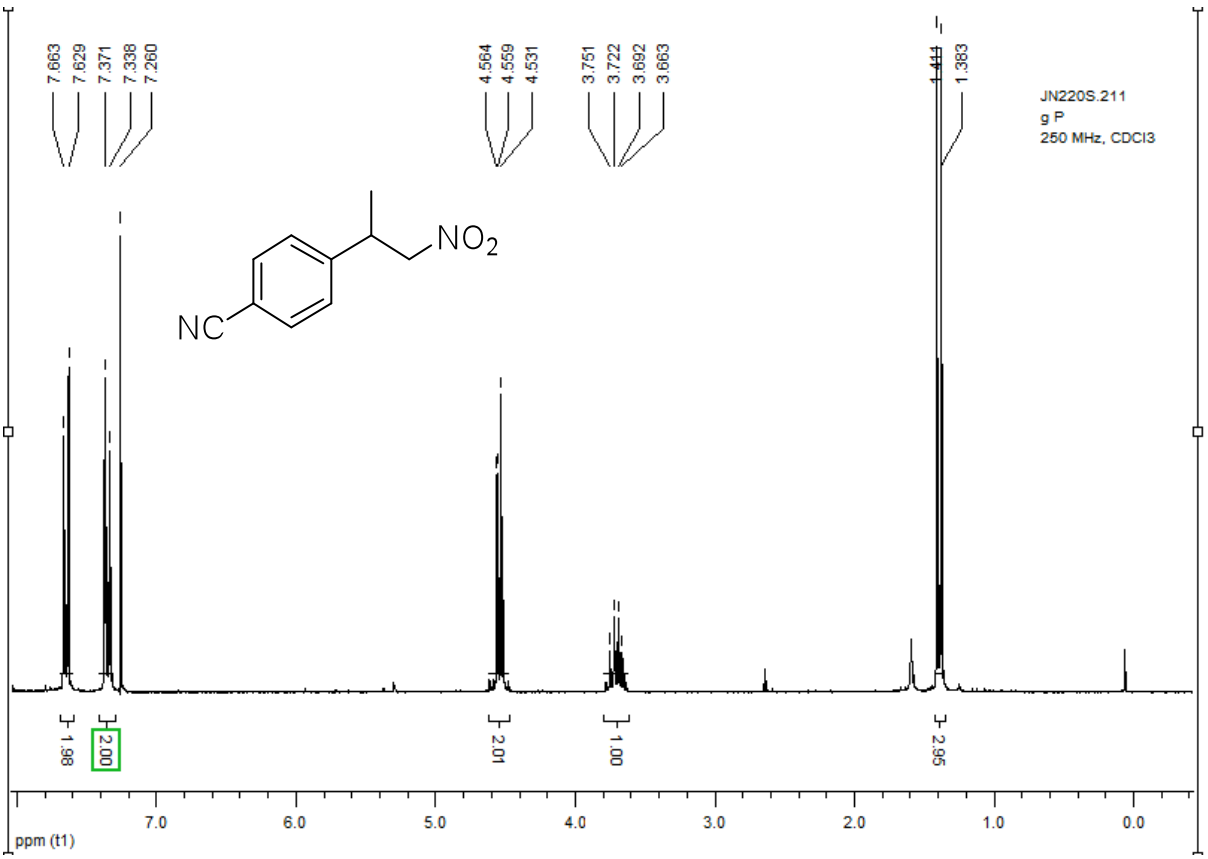

JN180S.137
63 MHz, CDCl3
139.307
133.407
129.146
128.269
81.559
77.508
77.283
77.000
76.492
38.068
18.712
NO2
Cl
150
100
50
0
ppm (t1)

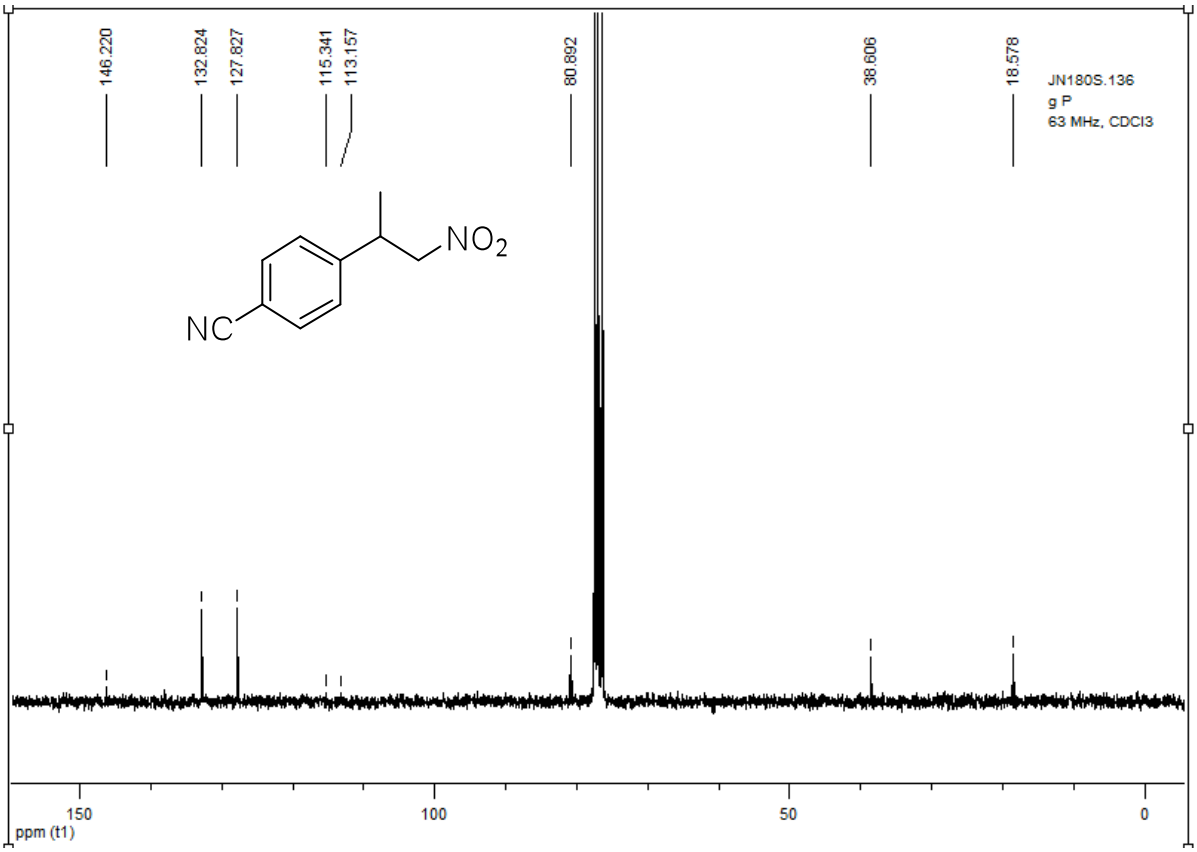
4e


7.255
7.223
7.202
7.188
7.176
7.167
7.052
7.017
6.982
4.508
4.499
4.477
4.468
3.666
3.637
3.608
3.578
1.370
1.342
JN170S.142
e P
250 MHz, CDCl3
NO2
F
2.11
1.97
2.01
0.99
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

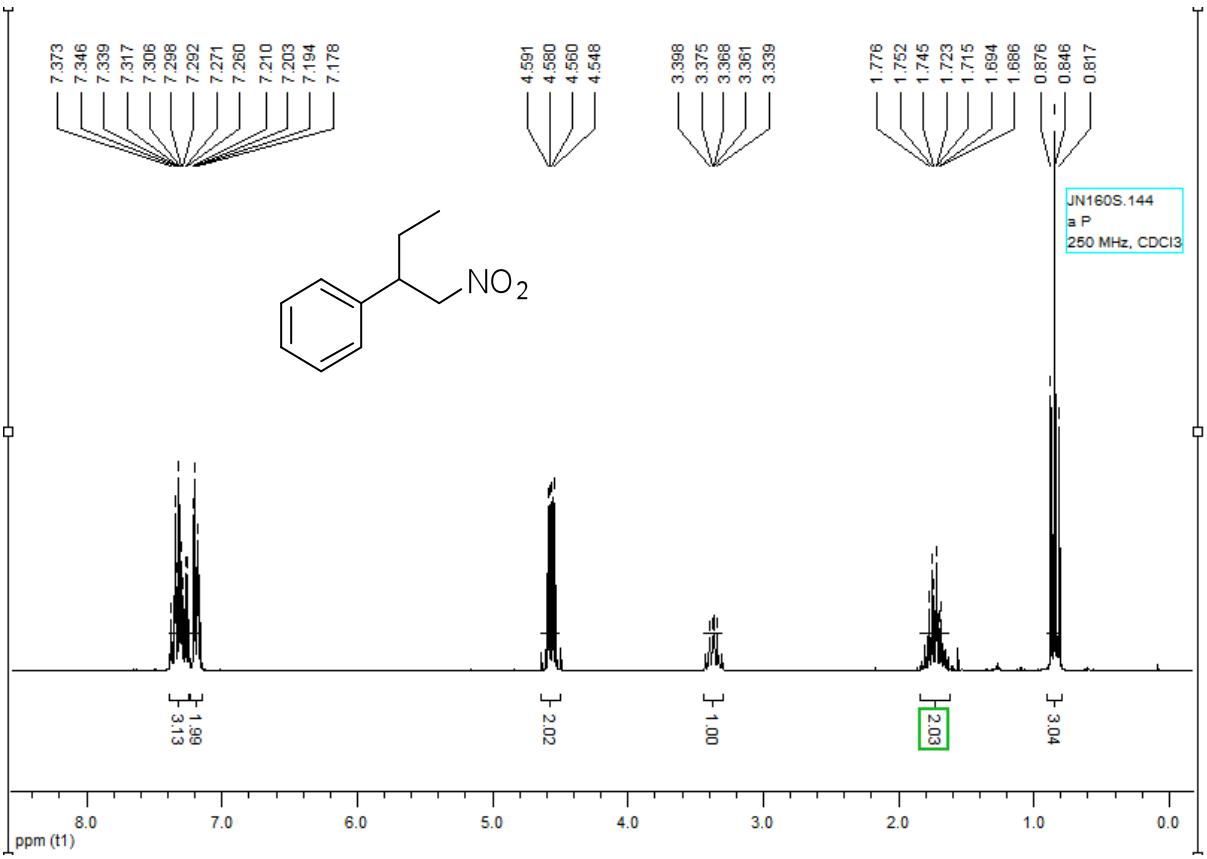

163.966
160.054
136.579
136.527
128.500
128.372
115.957
115.617
81.764
37.927
18.778
JN210S.210
e P
63 MHz, CDCl3
NO2
F
150
100
50
0
ppm (t1)

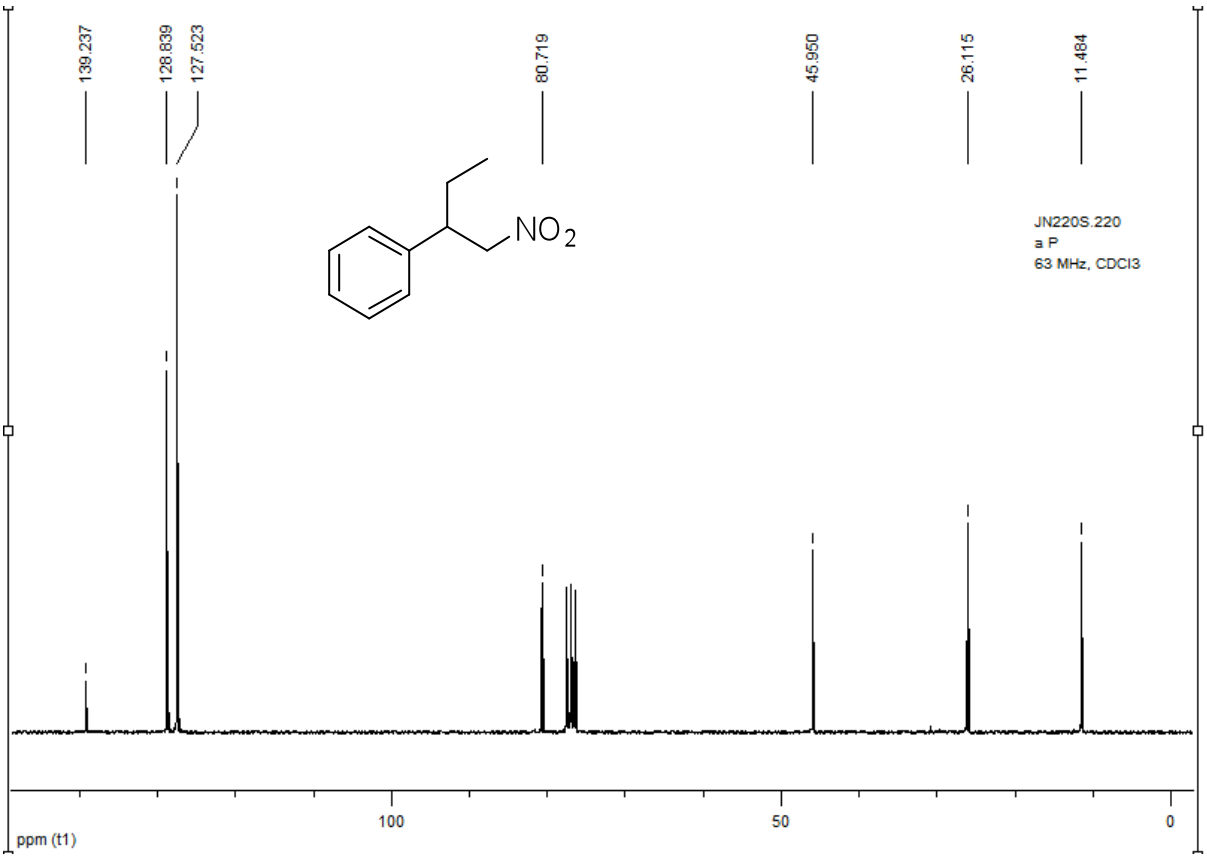
4f


7.663
7.629
7.371
7.338
7.260
4.564
4.559
4.531
3.751
3.722
3.692
3.663
1.414
1.383
JN220S.211
g P
250 MHz, CDCl3
NO2
NC
1.98
2.00
2.01
1.00
2.95
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

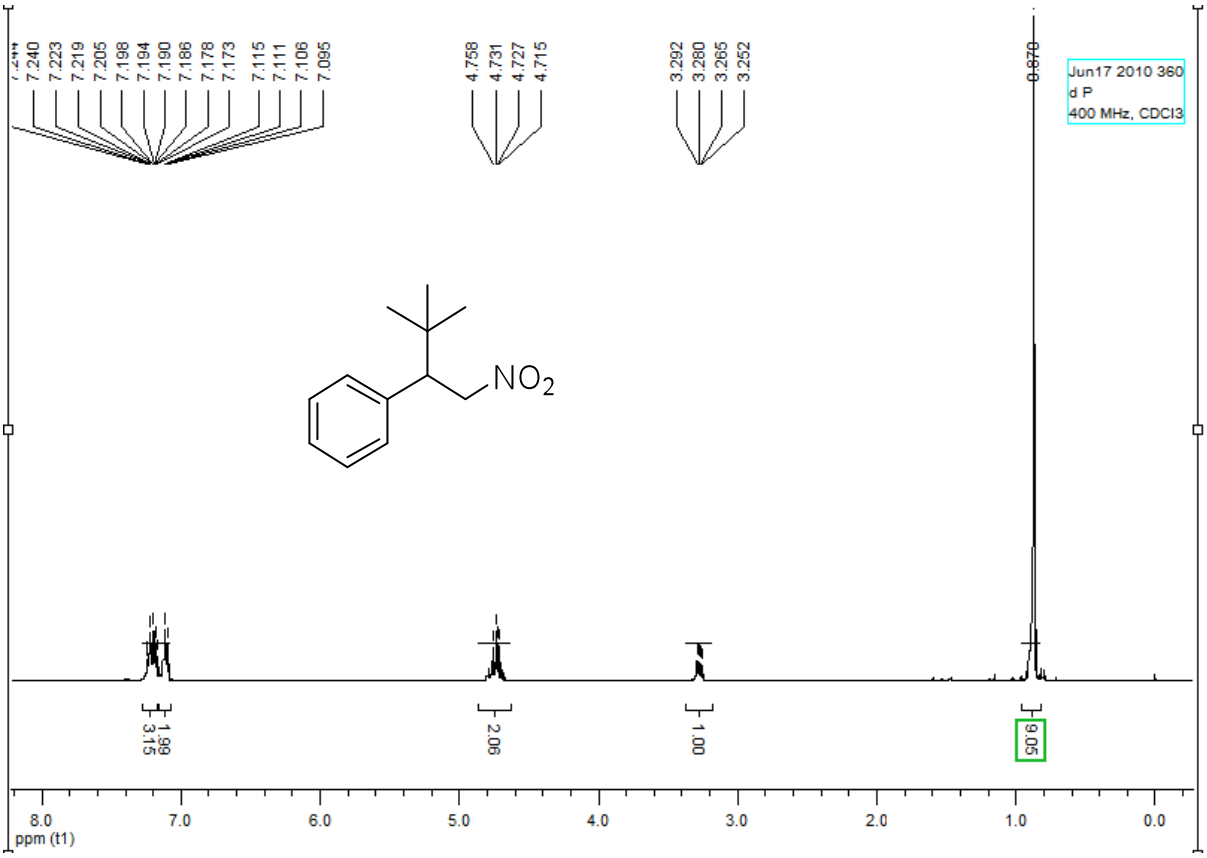

146.220
132.824
127.827
115.341
113.157
80.892
38.606
18.578
JN180S.136
g P
63 MHz, CDCl3
NO2
NC
150
100
50
0
ppm (t1)

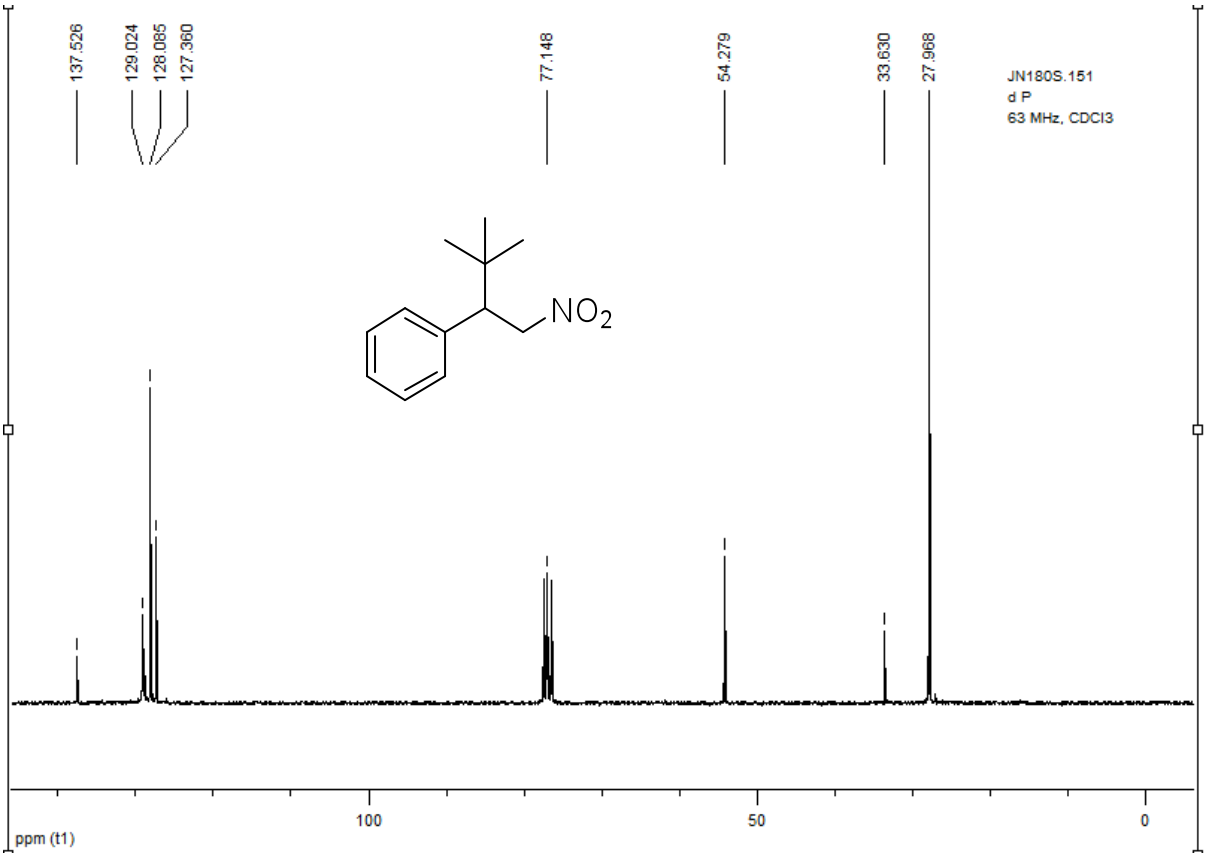
4g


7.373
7.346
7.339
7.317
7.306
7.298
7.292
7.271
7.260
7.210
7.203
7.194
7.178
4.591
4.580
4.560
4.548
3.398
3.375
3.368
3.361
3.339
1.776
1.752
1.745
1.723
1.715
1.694
1.686
0.876
0.846
0.817
JN160S.144
a P
250 MHz, CDCl3
NO2
3.13
1.99
2.02
1.00
2.03
3.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

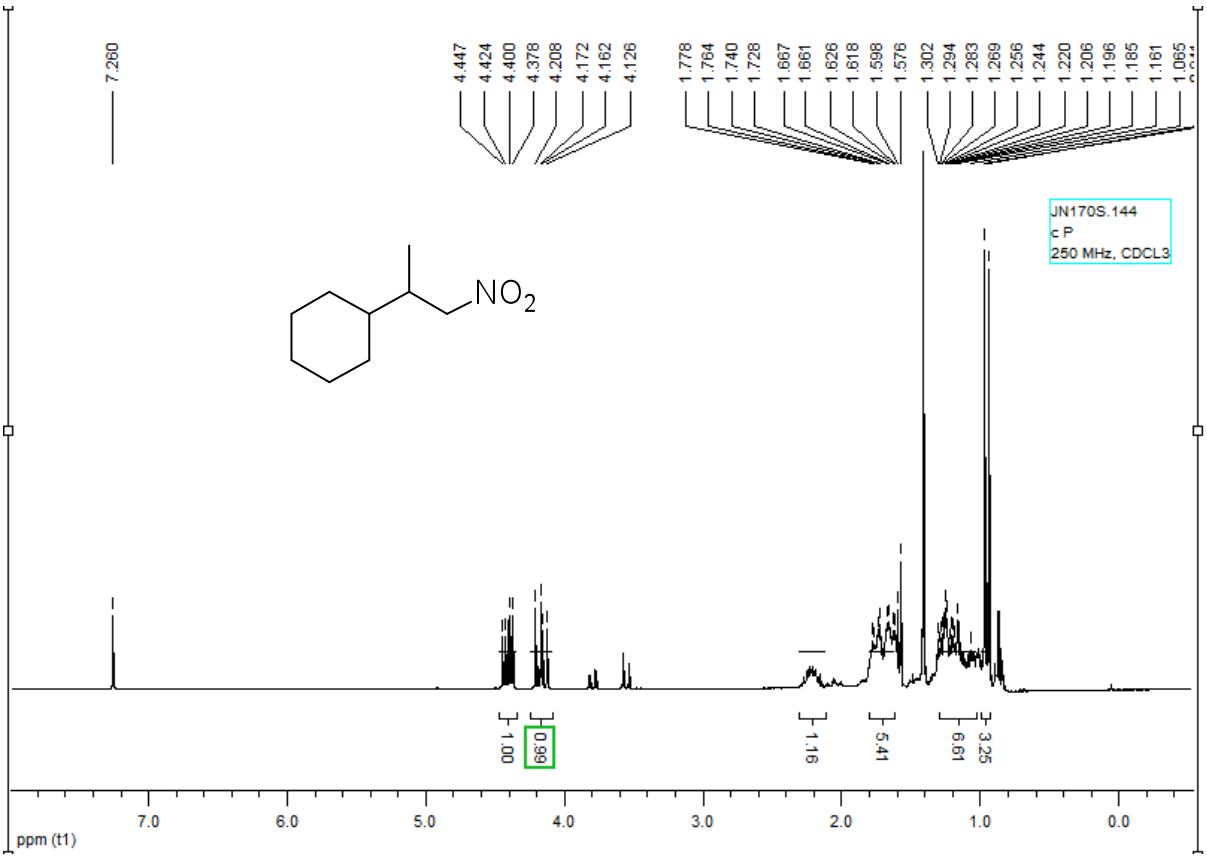

139.237
128.839
127.523
80.719
45.950
26.115
11.484
NO2
JN220S.220
a P
63 MHz, CDCl3
100
50
0
ppm (t1)

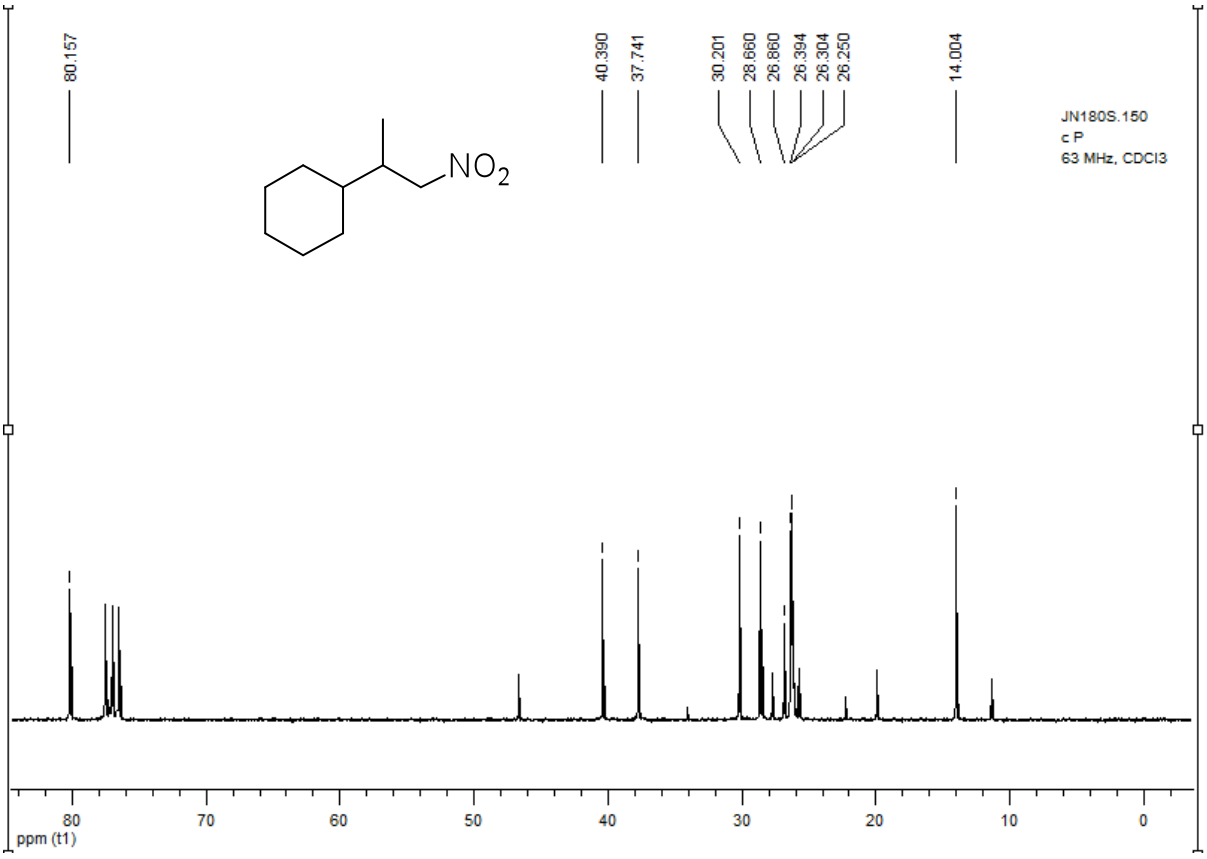
4h


7.240
7.223
7.219
7.205
7.198
7.194
7.190
7.186
7.178
7.173
7.115
7.111
7.106
7.095
4.758
4.731
4.727
4.715
3.292
3.280
3.265
3.252
0.870
Jun17 2010 360
d P
400 MHz, CDCl3
NO2
3.15
1.99
2.06
1.00
9.06
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

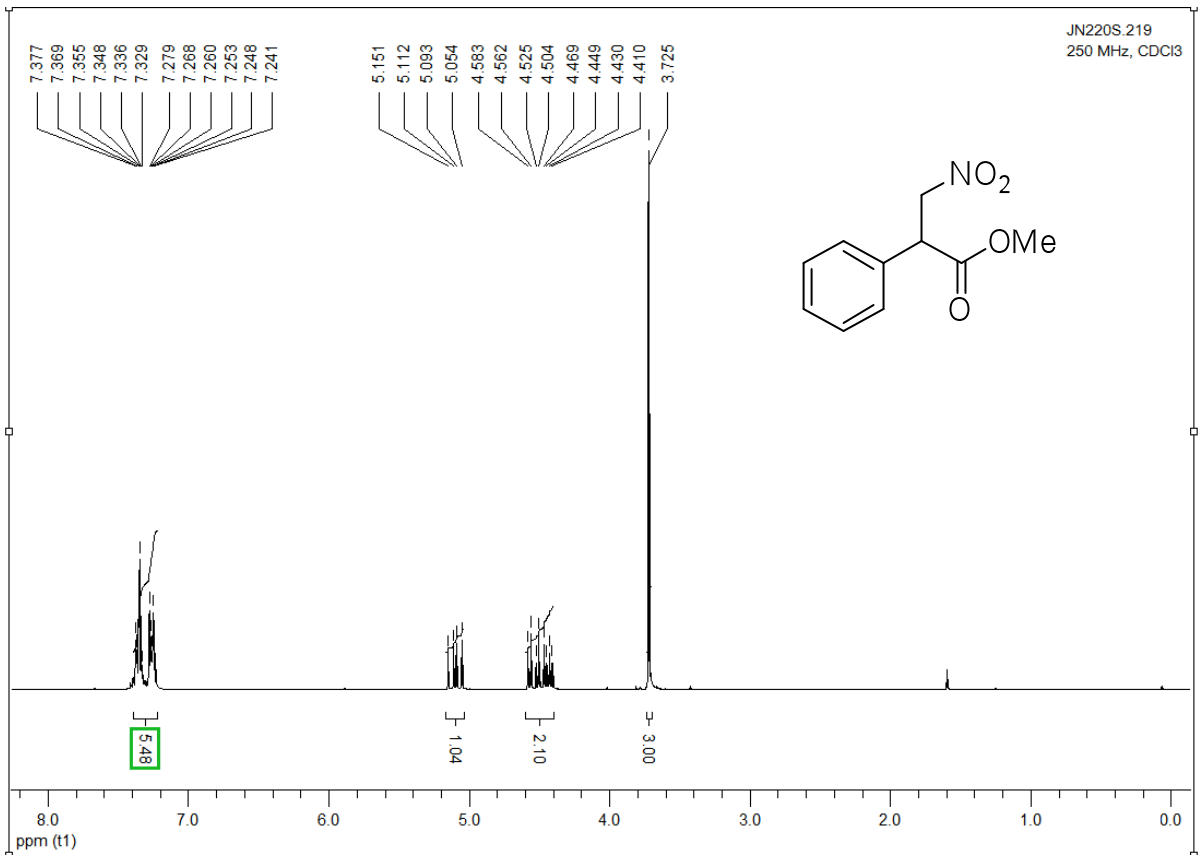

137.526
129.024
128.085
127.360
77.148
54.279
33.630
27.968
JN180S.151
d P
63 MHz, CDCl3
NO2
100
50
0
ppm (t1)

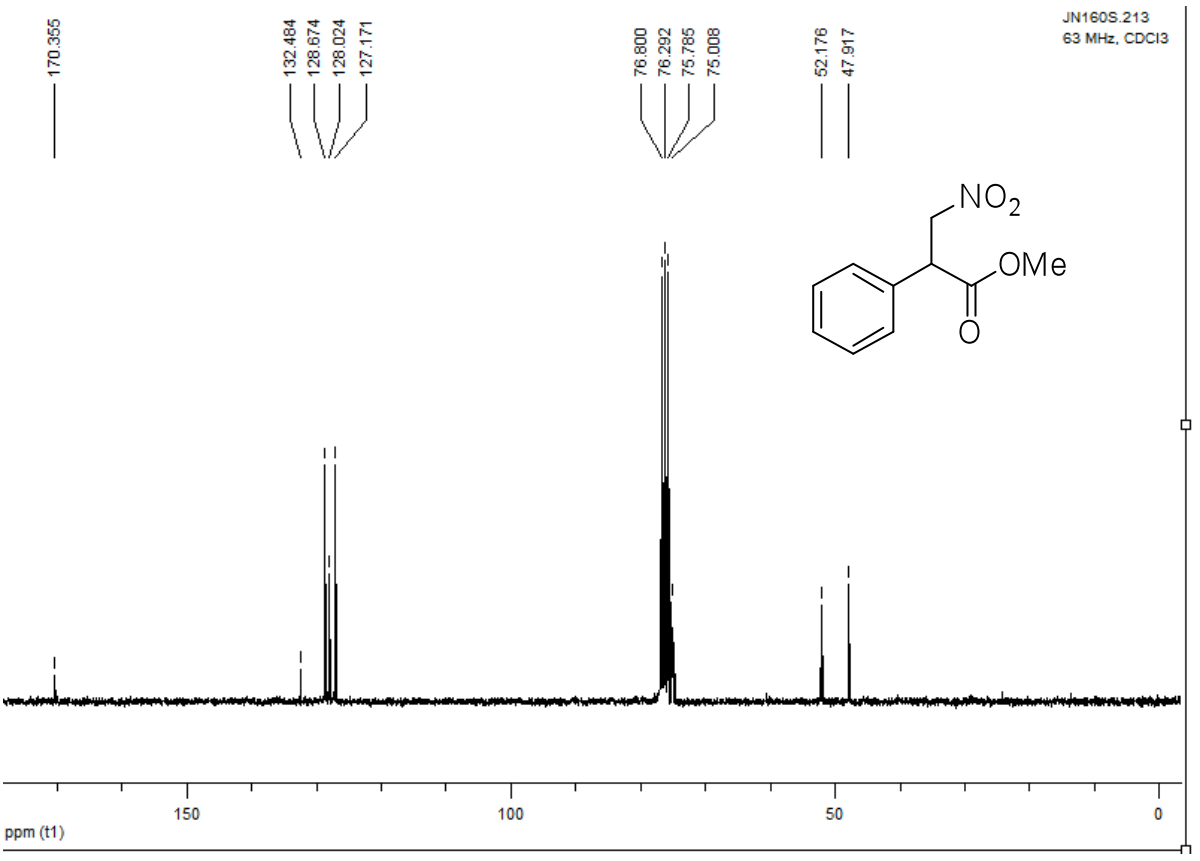
4i


7.260
4.447
4.424
4.400
4.378
4.208
4.172
4.162
4.126
1.778
1.764
1.740
1.728
1.667
1.661
1.626
1.618
1.598
1.576
1.302
1.294
1.283
1.269
1.256
1.244
1.220
1.206
1.196
1.185
1.161
1.065
JN170S.144
c P
250 MHz, CDCL3
NO2
1.00
0.99
1.16
5.41
6.61
3.25
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

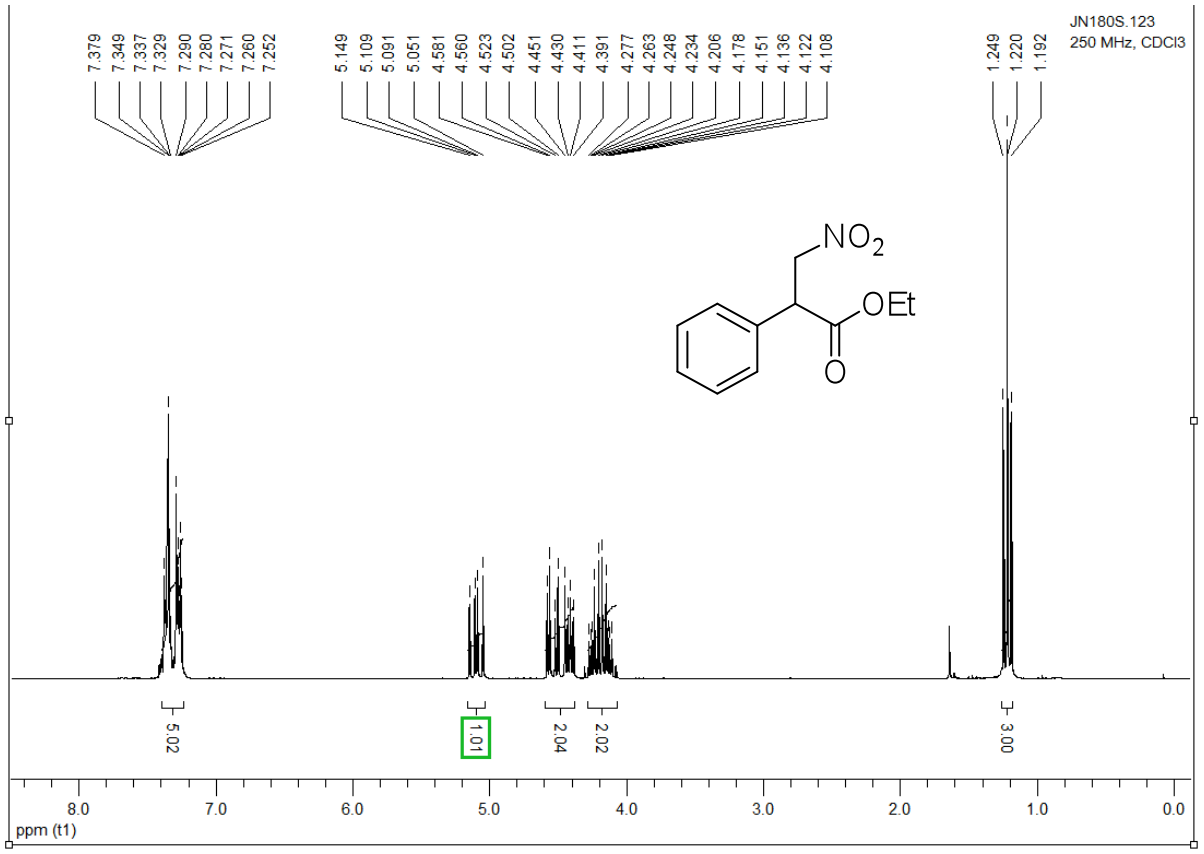

80.157
40.390
37.741
30.201
28.660
26.860
26.394
26.304
26.250
14.004
JN180S.150
c P
63 MHz, CDCl3
NO2
80
70
60
50
40
30
20
10
0
ppm (t1)

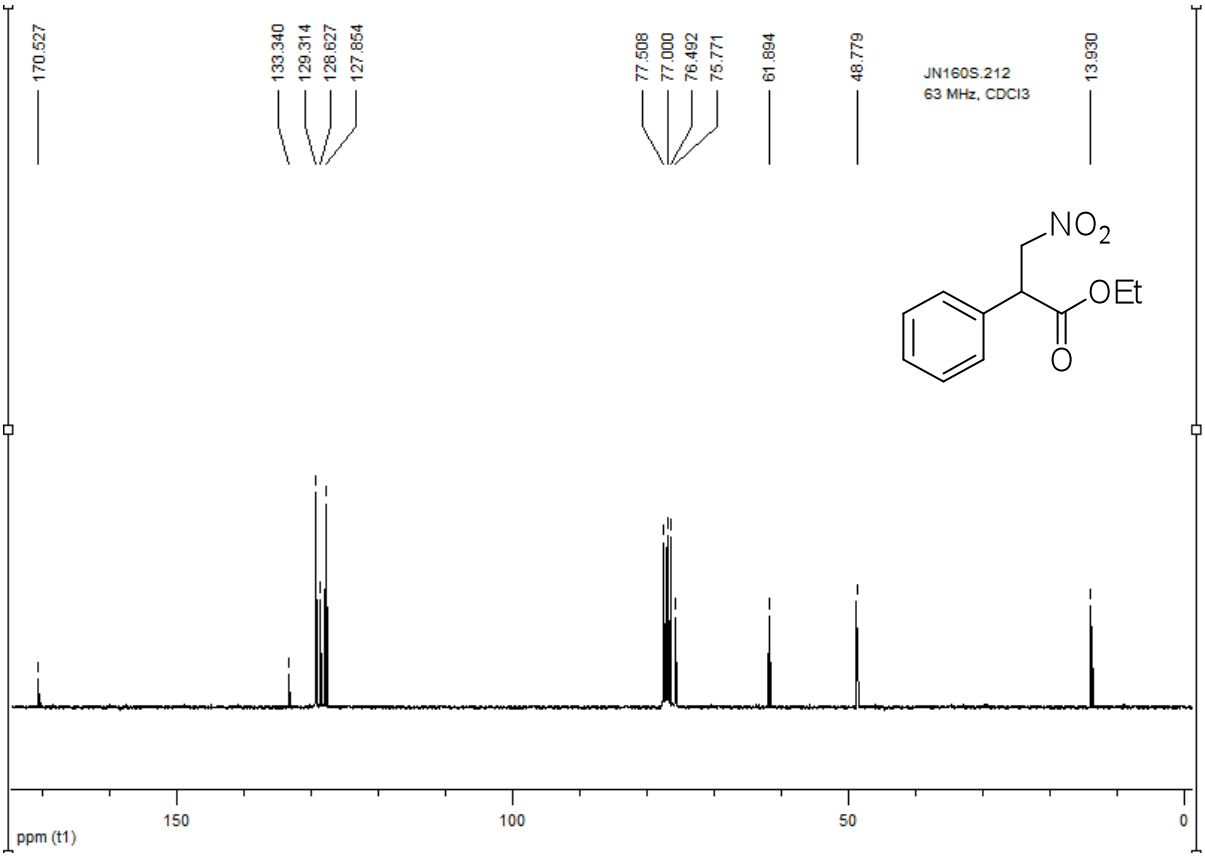
6a


JN220S.219
250 MHz, CDCl3
7.377
7.369
7.355
7.348
7.336
7.329
7.279
7.268
7.260
7.253
7.248
7.241
5.151
5.112
5.093
5.054
4.583
4.562
4.525
4.504
4.469
4.449
4.430
4.410
3.725
NO2
OMe
O
5.48
1.04
2.10
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

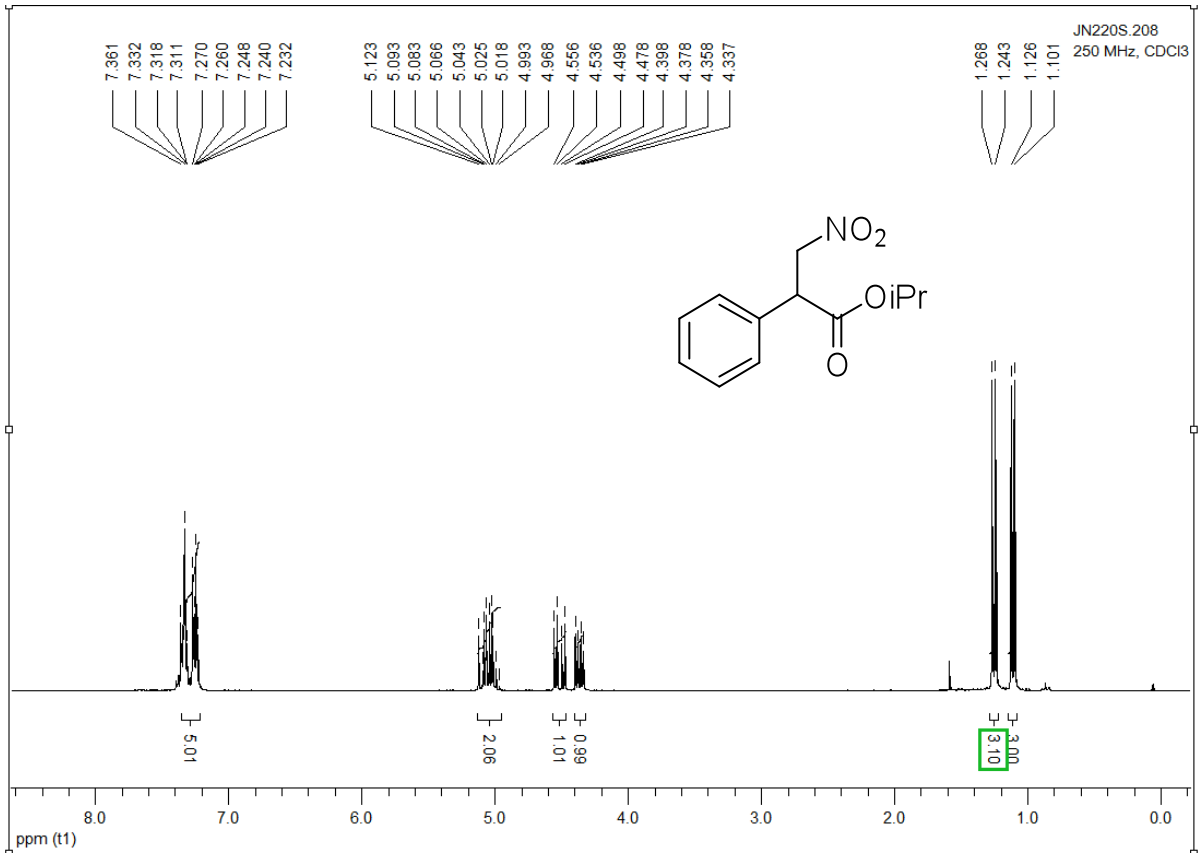

JN160S.213
63 MHz, CDCl3
170.355
132.484
128.674
128.024
127.171
76.800
76.292
75.785
75.008
52.176
47.917
NO2
OMe
O
150
100
50
0
ppm (t1)

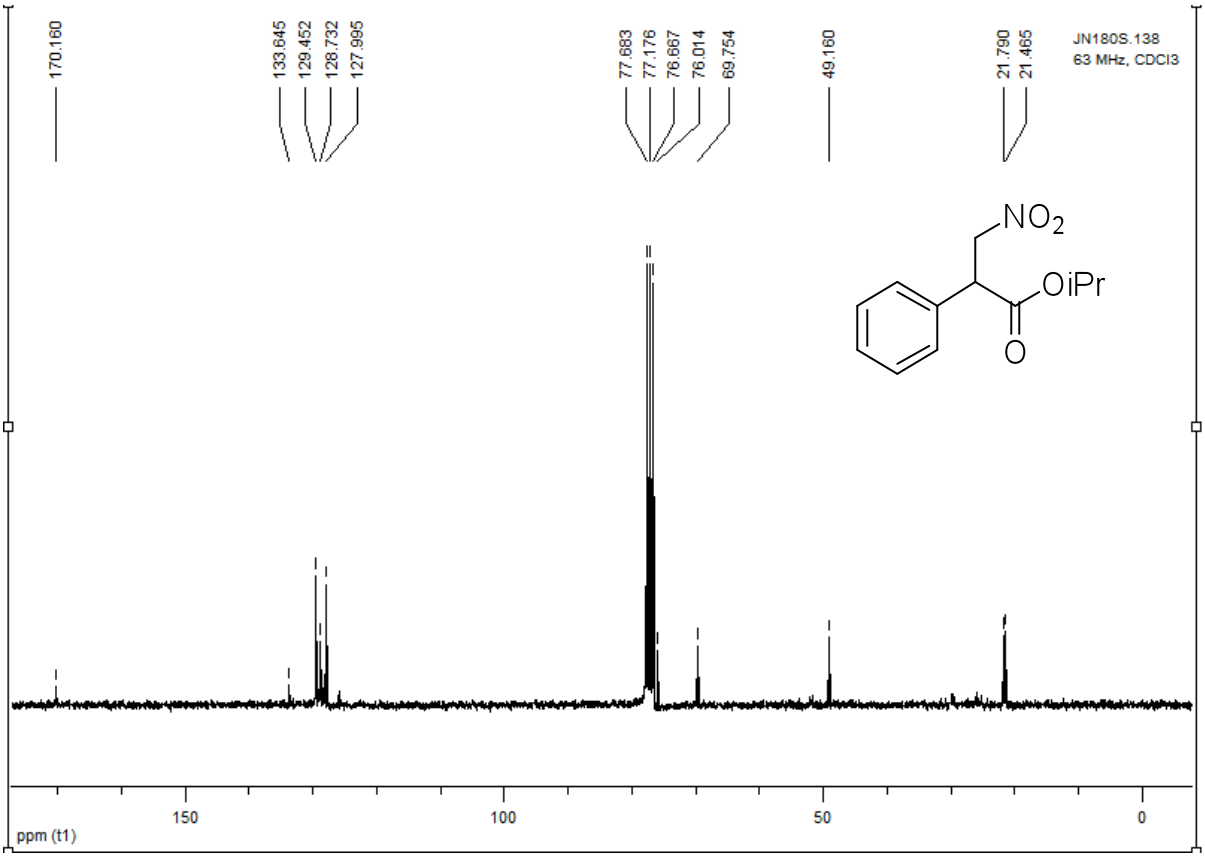
6b


JN180S.123
250 MHz, CDCl3
7.379
7.349
7.337
7.329
7.290
7.280
7.271
7.260
7.252
5.149
5.109
5.091
5.051
4.581
4.560
4.523
4.502
4.451
4.430
4.411
4.391
4.277
4.263
4.248
4.234
4.206
4.178
4.151
4.136
4.122
4.108
1.249
1.220
1.192
NO2
OEt
O
5.02
1.01
2.04
2.02
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


170.527
133.340
129.314
128.627
127.854
77.508
77.000
76.492
75.771
61.894
48.779
JN160S.212
63 MHz, CDCl3
13.930
NO2
OEt
O
150
100
50
0
ppm (t1)

6c


JN220S.208
250 MHz, CDCl3
7.361
7.332
7.318
7.311
7.270
7.260
7.248
7.240
7.232
5.123
5.093
5.083
5.066
5.043
5.025
5.018
4.993
4.968
4.556
4.536
4.498
4.478
4.398
4.378
4.358
4.337
1.268
1.243
1.126
1.101
NO2
OiPr
O
5.01
2.06
1.01
0.99
3.10
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


JN180S.138
63 MHz, CDCl3
170.160
133.645
129.452
128.732
127.995
77.683
77.176
76.667
76.014
69.754
49.160
21.790
21.465
NO2
OiPr
O
150
100
50
0
ppm (t1)