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Supporting Information

Novel Bifunctional Chiral Urea and Thiourea Derivatives as Organocatalysts. Enantioselective Nitro Michael Reaction of Malonates and Diketones

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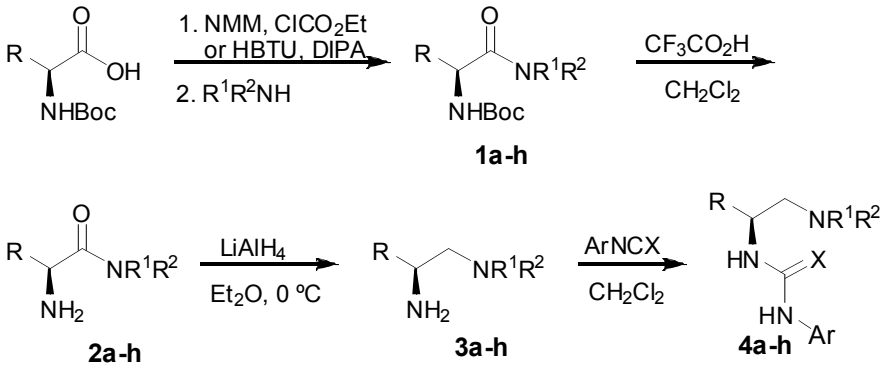
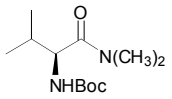
Experimental section

General information

^{1}H–NMR (300 MHz) and ^{13}C–NMR (75 MHz) spectra were recorded on a Bruker AC–300 or ARX–300 spectrometer in $CDCl_3$. Chemical shifts for protons are reported in ppm from tetramethylsilane with the residual $CHCl_3$ resonance as internal reference. Chemical shifts for carbons are reported in ppm from tetramethylsilane and are referenced to the carbon resonance of the solvent. Data are reported as follows: chemical shift, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, sp=septet, m=multiplet, br=broad), coupling constants in Hertz, and integration. Specific rotations were measured on a Perkin–Elmer digital polarimeter using a 5–mL cell with a 1–dm path length, and a sodium lamp, and concentration is given in g per 100 mL. Infrared spectra were recorded on a Perkin–Elmer FT–IR spectrometer and are reported in frequency of absorption. Melting points were obtained with open capillary tubes and are uncorrected. Flash chromatography was carried out using silica gel (230–240 mesh). Chemical yields refer to pure isolated substances. TLC analysis was performed on glass–backed plates coated with silica gel 60 and an F_{254} indicator, and visualized by either UV irradiation or by staining with I_2 or phosphomolybdic acid solution. Chiral HPLC analysis was performed on a Hewlett–Packard 1090 Series II instrument equipped with a quaternary pump, using a Daicel Chiralcel OD Column (250 × 4.6 mm) or Chiralpak AS–H, AD Column (250 × 4.6 mm). UV detection was monitored at 220 nm or at 254 nm. C, H and N elemental analyses were performed on a Perkin–Elmer 240 microanalyzer.
Unless otherwise indicated, all compounds were purchased from Aldrich and used as received. Nitroolefin **5f** was prepared according to the literature procedure[1]. Solvents were dried and stored over microwave–activated 4Å molecular sieves. All reactions were carried out under argon atmosphere.

Procedures for preparation of catalysts 4a–4h



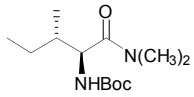


1a

(*S*)–*tert*–butyl 1–(dimethylamino)–3–methyl–1–oxobutan–2–ylcarbamate (1a).[2] To a solution of N–Boc–valine (4.35 g, 20 mmol) in dry THF (60 mL) was added 4–methylmorpholine (4.4 mL, 40 mmol) at –15 ºC under argon and then was added dropwise (for 10 minutes) a solution of ethyl chloroformate (1.9 mL, 20 mmol) in dry THF (10 mL). After stirring for 15 minutes was added dimethylamine hydrochloride (1.65 g, 20 mmol). The resulting mixture was allowed to warm to room temperature and stirred for 12 hours. The solvent was removed *in vacuo* and the resulting white solid was partitioned between EtOAc (60 mL) and 10% aqueous Na_2CO_3 (30 mL). The aqueous phase was separated and the organic layer was washed with

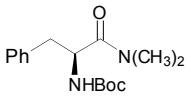
[1] S. E. Denmark, L. R. Marcin. *J. Org. Chem.* **1993**, *58*, 3850-3856
[2] A. R. Katritzky, Y.-J. Xu, H.-Y. He, P. J. Steel. *J. Chem. Soc., Perkin Trans. 1*, **2001**, 1767-1770

0.1M HCl (30 mL) and brine (30 mL), and was dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (ethyl acetate/hexane = 4/1) to afford compound **1a** (3.42 g, 14.0 mmol, 70%). Colorless oil. $[\alpha]_D^{25}$=+31.1 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.89 (d, *J*=6.7 Hz, 3H), 0.95 (d, *J*=6.8 Hz, 3H), 1.42 (s, 9H), 1.90–1.96 (m, 1H), 2.96 (s, 3H), 3.09 (s, 3H), 4.46 (dd, *J*=9.1, 5.9 Hz, 1H), 5.33 (d, *J*=9.0 Hz, 1H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 16.7 (CH_3), 18.8 (CH_3), 27.6 (3 CH_3), 30.7 (CH), 34.8 (CH_3), 36.6 (CH_3), 54.3 (CH), 78.3 (C), 155.2 (C), 171.5 (C); **IR** (film) ν 3301, 2970, 1785, 1709, 1644, 1498, 1248, 1174.



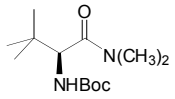
1b

(2*S*,3*S*)–*tert*–butyl 1–(dimethylamino)–3–methyl–1–oxopentan–2–ylcarbamate (1b). This compound was obtained from N–Boc–isoleucine (701 mg, 3 mmol) by the method described for **1a** and purified by flash chromatography (ethyl acetate/hexane = 3/1): 413 mg (1.6 mmol, 53% yield). Colorless oil. $[\alpha]_D^{25}$=+16.0 (*c*=0.9, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.81–0.88 (m, 6H), 1.02–1.12 (m, 1H), 1.37 (s, 9H), 1.44–1.53 (m, 1H), 1.59–1.68 (m, 1H), 2.92 (s, 3H), 3.07 (s, 3H), 4.44 (dd, *J*=9.2, 6.8 Hz, 1H), 5.30 (d, *J*=9.2 Hz, 1H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 11.1 (CH_3), 15.4 (CH_3), 23.8 (CH_2), 28.1 (3 CH_3), 35.4 (CH_3), 37.2 (CH_3), 37.9 (CH), 54.1 (CH), 79.1 (C), 155.6 (C), 172.3 (C); **IR** (film) ν 3300, 2968, 1786, 1710, 1644, 1497.



1c

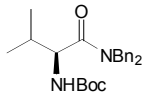
(*S*)–*tert*–butyl 1–(dimethylamino)–1–oxo–3–phenylpropan–2–ylcarbamate (1c). This compound was obtained from N–Boc–phenylalanine (804 mg, 3 mmol) by the method described for **1a** and purified by flash chromatography (ethyl acetate/hexane = 2/1): 698 mg (2.4 mmol, 80% yield). Colorless oil. $[\alpha]_D^{25}$=+32.8 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.41 (s, 9H), 2.62 (s, 3H), 2.85 (s, 3H), 2.89–2.97 (m, 2H), 4.78–4.86 (m, 1H), 5.45 (d, *J*=8.9 Hz, 1H), 7.17–7.22 (m, 2H), 7.23–7.32 (m, 3H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 27.9 (3 CH_3), 35.0 (CH_3), 36.3 (CH_3), 39.6 (CH_2), 51.0 (CH), 78.8 (C), 126.3 (CH), 127.8 (2 CH), 128.9 (2 CH), 136.2 (C), 154.7 (C), 171.1 (C); **IR** (film) ν 3261, 2974, 1787, 1708, 1644, 1498, 1367, 1172.



1d

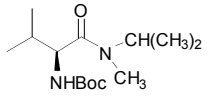
(*S*)–*tert*–butyl 1–(dimethylamino)–3,3–dimethyl–1–oxobutan–2–ylcarbamate (1d).[3] To a solution of N–Boc–*tert*–leucine (1.5 mmol, 350 mg) in dry CH_2Cl_2 (12 mL) was added HBTU (1.5 mmol, 580 mg) under argon. After 2 minutes diisopropylethylamine (4.5 mmol, 0.79 mL) and dimethylamine hydrochloride (125 mg, 1.5 mmol) were added sequentially and the reaction was stirred for 90 min. The mixture was combined with dichloromethane (10 mL) and water (10 mL) and the organic layer was separated, washed three times with 1M HCl (10 mL), and dried over $MgSO_4$. Solvents were removed *in vacuo* to afford a mixture of the product and tetramethylurea as a colorless oil, which was purified by flash chromatography (ethyl acetate/hexane = 4/1). A colorless oil was obtained in quantitative yield (1.5 mmol, 388 mg). $[\alpha]_D^{25}$=+29.4 (*c*=1.1, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.95 (s, 9H), 1.40 (s, 9H), 2.94 (s, 3H), 3.11 (s, 3H), 4.51 (d, *J*=9.7 Hz, 1H), 5.32 (d, *J*=9.4 Hz, 1H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 26.0 (3 CH_3), 28.0 (3 CH_3), 35.1 (CH_3), 35.3 (C), 37.9 (CH_3), 55.4 (CH), 78.8 (C), 155.3 (C), 171.5 (C); **IR** (film) ν 3314, 2969, 1712, 1642, 1498, 1397, 1367, 1247, 1193.

[3] P. Vachal, E. N. Jacobsen. *J. Am. Chem. Soc.*, **2002**, *124*, 10012-10014



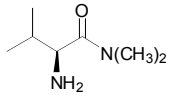
1f

(*S*)–*tert*–butyl 1–(dibenzylamino)–3–methyl–1–oxobutan–2–ylcarbamate (1f). This compound was obtained from N–Boc–valine (435 mg, 2 mmol) and dibenzylamine by the method described for **1a** and purified by flash chromatography (ethyl acetate/hexane = 8/1): 531 mg (1.3 mmol, 67% yield). White solid. $[\alpha]_D^{25}$=–43.3 (*c*=1.0, $CHCl_3$); **m.p.** (hexane/EtOAc)=142–143 ºC; **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.92 (d, *J*=6.7 Hz, 3H), 0.96 (d, *J*=6.7 Hz, 3H), 1.46 (s, 9H), 1.99–2.10 (m, 1H), 4.31 (d, *J*=14.8 Hz, 1H), 4.47 (d, *J*=16.5 Hz, 1H), 4.56–4.67 (m, 2H), 4.87 (d, *J*=14.7 Hz, 1H), 5.40 (d, *J*=9.2 Hz, 1H), 7.18–7.26 (m, 4H), 7.29–7.39 (m, 6H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 17.1 (CH_3), 19.3 (CH_3), 27.9 (3 CH_3), 31.2 (CH), 47.3 (CH_2), 49.5 (CH_2), 55.0 (CH), 78.8 (C), 126.9 (2 CH), 127.0 (CH), 127.3 (CH), 127.8 (2 CH), 128.2 (2 CH), 128.4 (2 CH), 135.8 (C), 136.7 (C), 155.4 (C), 172.4 (C); **IR** (KBr) ν 3292, 2976, 1707, 1624, 1528, 1452, 1172.



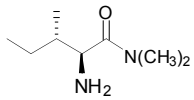
1g

(S)–tert–butyl 1–(isopropyl(methyl)amino)–3–methyl–1–oxobutan–2–ylcarbamate (1g). This compound was obtained from N–Boc–valine (435 mg, 2 mmol) and dibenzylamine by the method described for **1a** and purified by flash chromatography (ethyl acetate/hexane = 5/1): 236 mg (0.9 mmol, 43% yield). Colorless oil. $[\alpha]_D^{25}$=+16.8 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$, 2 rotamers) δ 0.89 (d, *J*=6.8 Hz, 3H), 0.93–0.97 (m, 3H), 1.08–1.11 (m, 3H), 1.18–1.23 (m, 3H), 1.43 (s, 9H), 1.92 (sp, *J*=6.3 Hz, 1H), 2.79 (s, 1.2H), 2.90 (s, 1.8H), 4.22 (sp, *J*=6.6 Hz, 0.4H), 4.41 (dd, *J*=9.2, 5.9 Hz, 0.6H), 4.49 (dd, *J*=9.3, 6.0 Hz, 0.4H), 4.85 (sp, *J*=6.8 Hz, 0.6H), 5.34 (d, *J*=7.7 Hz, 1H),; **^{13}C–NMR** (75 MHz, $CDCl_3$, 2 rotamers) δ 17.1 (CH_3), 18.9 (CH_3), 19.3 (CH_3), 19.4 (CH_3), 19.6 (CH_3), 20.3 (CH_3), 20.5 (CH_3), 25.9 (CH_3), 28.2 (3 CH_3), 31.4 (CH), 31.7 (CH), 44.2 (CH), 47.7 (CH), 54.9 (CH), 55.3 (CH), 79.1 (C), 155.7 (C), 155.8 (C), 171.5 (C); **IR** (film) ν 3433, 3301, 2974, 1712, 1633, 1498, 1175.



2a

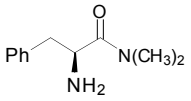
(*S*)–2–amino–N,N,3–trimethylbutanamide (2a). The N–Boc–aminoamide **1a** (978 mg, 4 mmol) was dissolved in a mixture of CH_2Cl_2 / TFA (4:1) (10 mL) and stirred at room temperature until disappearance of the starting material by TLC (1–3 hours). The mixture was diluted with CH_2Cl_2, cooled to 0 ºC and basified with saturated aqueous solution of $NaHCO_3$ (Gas evolution!). The biphasic mixture is extracted with CH_2Cl_2 (10 × 4 mL) and the combined organic extracts were dried over anhydrous $MgSO_4$. After removal of the solvent at reduced pressure the aminoamide **2a** was obtained in 91% yield (592 mg, 3.6 mmol). The crude product may be used directly in the next step. Colorless oil. $[\alpha]_D^{25}$=+69.6 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.91 (d, *J*=6.7 Hz, 3H), 0.97 (d, *J*=6.8 Hz, 3H), 1.82–1.93 (m, 1H), 2.12 (br s, 2H), 2.97 (s, 3H), 3.04 (s, 3H), 3.55 (d, *J*=5.3 Hz, 1H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 16.2 (CH_3), 19.3 (CH_3), 31.3 (CH), 35.0 (CH_3), 36.4 (CH_3), 55.5 (CH), 174.4 (C); **IR** (film) ν 3377, 2964, 1636.



2b

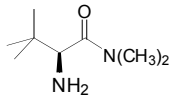
(2*S*,3*S*)–2–amino–N,N,3–trimethylpentanamide (2b). This compound was obtained from N–Boc–aminoamide **1b** (349 mg, 1.35 mmol) by the method described for **2a**: 239 mg (1.35 mmol,

quantitative yield). Colorless oil. $[\alpha]_D^{25}$=+45.9 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.90 (t, *J*=7.3 Hz, 3H), 0.96 (d, *J*=6.7 Hz, 3H), 1.08–1.25 (m, 1H), 1.55–1.69 (m, 2H), 2.98 (s, 3H), 3.05 (s, 3H), 3.17 (br s, 2H), 3.69 (d, *J*=5.1 Hz, 1H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 11.0 (CH_3), 15.7 (CH_3), 23.1 (CH_2), 35.3 (CH_3), 36.8 (CH_3), 38.4 (CH), 55.1 (CH), 174.7 (C); **IR** (film) ν 2967, 1654, 1202, 1132.



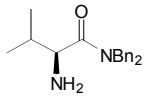
2c

(*S*)–2–amino–N,N–dimethyl–3–phenylpropanamide (2c). This compound was obtained from N–Boc–aminoamide **1c** (1.17 g, 4 mmol) by the method described for **2a**: 677 mg (3.5 mmol, 88% yield). Colorless oil. $[\alpha]_D^{25}$=+43.9 (*c*=0.8, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.94 (br s, 2H), 2.73 (s, 3H), 2.75–2.84 (m, 1H), 2.90 (s, 3H), 2.90–2.96 (m, 1H), 3.94 (t, *J*=6.9 Hz, 1H), 7.17–7.21 (m, 2H), 7.21–7.32 (m, 3H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 35.0 (CH_3), 35.9 (CH_3), 41.9 (CH_2), 51.9 (CH), 126.0 (CH), 127.8 (2 CH), 128.6 (2 CH), 137.0 (C), 173.7 (C); **IR** (film) ν 3367, 3028, 2930, 1636, 734, 702.



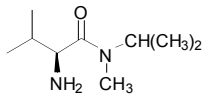
2d

(*S*)–2–amino–N,N,3,3–tetramethylbutanamide (2d). This compound was obtained from N–Boc–aminoamide **1d** (258 mg, 1 mmol) by the method described for **2a**: 158 mg (1 mmol, quantitative yield). Colorless oil. $[\alpha]_D^{25}$=+94.8 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.94 (s, 9H), 2.00 (br s, 2H), 2.94 (s, 3H), 3.05 (s, 3H), 3.53 (s, 1H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 25.7 (3 CH_3), 34.7 (C), 35.0 (CH_3), 37.5 (CH_3), 56.8 (CH), 173.8 (C); **IR** (film) ν 3386, 2954, 1637.



2f

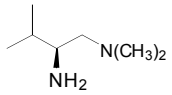
(*S*)–2–amino–N,N–dibenzyl–3–methylbutanamide (2f). This compound was obtained from N–Boc–aminoamide **1f** (531 mg, 1.3 mmol) by the method described for **2a**: 392 mg (1.3 mmol, quantitative yield). Colorless oil. $[\alpha]_D^{25}$=–12.8 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.02 (d, *J*=7.6 Hz, 3H), 1.05 (d, *J*=7.3 Hz, 3H), 2.04–2.15 (m, 1H), 3.99–4.06 (m, 1H), 4.02 (d, *J*=14.7 Hz, 1H), 4.26 (d, *J*=16.6 Hz, 1H), 4.59 (d, *J*=16.7 Hz, 1H), 5.01 (d, *J*=14.8 Hz, 1H), 5.56 (br s, 2H), 7.10–7.26 (m, 4H), 7.27–7.44 (m, 6H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 16.3 (CH_3), 19.6 (CH_3), 31.2 (CH), 47.8 (CH_2), 49.5 (CH_2), 56.1 (CH), 126.7 (2 CH), 127.4 (CH), 127.8 (CH), 128.1 (2 CH), 128.5 (2 CH), 128.9 (2 CH), 135.5 (C), 136.7 (C), 172.9 (C); **IR** (film) ν 3065, 2966, 1648, 1202



2g

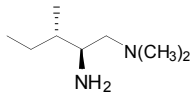
(S)–2–amino–N–isopropyl–N,3–dimethylbutanamide (2g). This compound was obtained from N–Boc–aminoamide **1g** (236 mg, 0.9 mmol) by the method described for **2a**: 145 mg (0.9 mmol, quantitative yield). Colorless oil. $[\alpha]_D^{25}$=+58.5 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$, 2 rotamers) δ 0.88–0.92 (m, 3H), 0.94–0.97 (m, 3H), 1.07–1.10 (m, 3H), 1.17–1.22 (m, 3H), 1.66 (br s, 2H), 1.83 (sp, *J*=6.6 Hz, 1H), 2.79 (s, 1.2H), 2.83 (s, 1.8H), 3.43 (d, *J*=5.7 Hz, 0.6H), 3.50 (d, *J*=5.3 Hz, 0.4H), 4.09 (sp, *J*=6.6 Hz, 0.4H), 4.89 (sp, *J*=6.8 Hz, 0.6H); **^{13}C–NMR** (75 MHz, $CDCl_3$, 2 rotamers) δ 16.4 (CH_3), 16.7 (CH_3), 18.9 (CH_3), 19.3 (CH_3), 19.7 (CH_3), 20.0

(CH_3), 20.3 (CH_3), 20.4 (CH_3), 25.8 (CH_3), 27.8 (CH_3), 31.8 (CH), 32.0 (CH), 44.0 (CH), 47.1 (CH), 56.3 (CH), 56.6 (CH), 174.3 (C); **IR** (film) ν 3378, 2967, 1632, 1466, 1113, 754



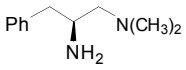
3a

(*S*)–N1,N1,3–trimethylbutane–1,2–diamine (3a). To a 0 ºC cooled suspension of LAH (1.20 g, 30 mmol) in dry diethyl ether was added dropwise a solution of amide **2a** (1.44 g, 10 mmol) in dry diethyl ether (10 mL) under argon. The mixture was stirred at 0 ºC until disappearance of the starting material (TLC) (1–3 hours) and carefully quenched by sequential addition of water (1.2 mL), 15% NaOH (1.2 mL) and water (3.6 mL). The solids were filtered off and washed with diethyl ether, and the filtrate was dried over $MgSO_4$. The solvent was removed *in vacuo* to afford the amine as a yellow liquid in 95% yield (1.24 g, 9.5 mmol). The crude product may be used directly in the next step. $[\alpha]_D^{25}$=+54.6 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.90 (d, *J*=3.3 Hz, 3H), 0.92 (d, *J*=3.2 Hz, 3H), 1.50–1.61 (m, 1H), 1.73 (br s, 2H), 2.09–2.21 (m, 2H), 2.22 (s, 6H), 2.62–2.68 (m, 1H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 17.8 (CH_3), 19.3 (CH_3), 32.0 (CH), 45.8 (2 CH_3), 53.6 (CH), 64.5 (CH_2); **IR** (film) ν 3368, 2958, 1466.



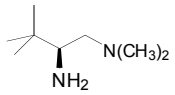
3b

(2*S*,3*S*)–N1,N1,3–trimethylpentane–1,2–diamine (3b). This compound was obtained from aminoamide **2b** (139 mg, 0.9 mmol) by the method described for **3a**: 87 mg (0.6 mmol, 69% yield). Yellow liquid. $[\alpha]_D^{25}$=+30.7 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.82–0.95 (m, 6H), 1.10–1.27 (m, 1H), 1.29–1.37 (m, 1H), 1.42–1.54 (m, 1H), 1.65 (br s, 2H), 2.07–2.31 (m, 2H), 2.21 (s, 6H), 2.70–2.77 (m, 1H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 11.5 (CH_3), 14.9 (CH_3), 25.0 (CH_2), 38.9 (CH), 45.7 (2 CH_3), 52.2 (CH), 63.8 (CH_2); **IR** (film) ν 3364, 2962, 1459.



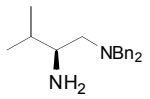
3c

(*S*)–N^1,N^1–dimethyl–3–phenylpropane–1,2–diamine (3c). This compound was obtained from aminoamide **2c** (365 mg, 1.9 mmol) by the method described for **3a**: 323 mg (1.8 mmol, 96% yield). Yellow liquid. $[\alpha]_D^{25}$=+6.2 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.74 (br s, 2H), 2.14–2.20 (m, 1H), 2.24 (s, 6H), 2.27–2.32 (m, 1H), 2.48 (dd, *J*=13.3, 8.7 Hz, 1H), 2.75 (dd, *J*=13.2, 4.4 Hz, 1H), 3.10–3.19 (m, 1H), 7.20–7.26 (m, 3H), 7.27–7.33 (m, 2H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 41.9 (CH_2), 45.5 (2 CH_3), 49.7 (CH), 66.0 (CH_2), 125.9 (CH), 128.1 (2 CH), 129.0 (2 CH), 138.9 (C); **IR** (film) ν 3368, 2928, 1458, 701.



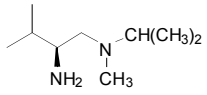
3d

(*S*)–N^1,N^1,3,3–tetramethylbutane–1,2–diamine (3d). This compound was obtained from aminoamide **2d** (167 mg, 1.1 mmol) by the method described for **3a**: 146 mg (1.0 mmol, 96% yield). Yellow liquid. $[\alpha]_D^{25}$=+58.8 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.85 (s, 9H), 1.58 (br s, 2H), 2.09–2.12 (m, 2H), 2.18 (s, 6H), 2.53 (dd, *J*=8.8, 4.5 Hz, 1H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 26.0 (3 CH_3), 32.8 (C), 45.6 (2 CH_3), 56.7 (CH), 61.7 (CH_2); **IR** (film) ν 3370, 2953, 1458, 1037, 755.



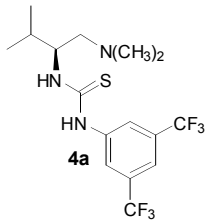
3f

(*S*)–N^1,N^1–dibenzyl–3–methylbutane–1,2–diamine (3f). This compound was obtained from aminoamide **2f** (468 mg, 1.6 mmol) by the method described for **3a**: 384 mg (1.6 mmol, 98% yield). Colorless oil. **[α]$_D^{25}$**=+73.0 (*c*=1.2, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.82 (d, *J*=6.7 Hz, 3H), 0.89 (d, *J*=6.8 Hz, 3H), 1.51–1.59 (m, 3H), 2.32 (dd, *J*=12.4, 9.7 Hz, 1H), 2.46 (dd, *J*=12.5, 3.8 Hz, 1H), 2.70–2.77 (m, 1H), 3.40 (d, *J*=13.5 Hz, 2H), 3.78 (d, *J*=13.5 Hz, 2H), 7.23–7.38 (m, 10H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 17.7 (CH_3), 19.4 (CH_3), 31.6 (CH), 53.7 (CH), 58.7 (2 CH_2), 126.8 (2 CH), 128.1 (4 CH), 128.9 (4 CH), 139.2 (2 C); **IR** (film) ν 3376, 2957, 1495, 1453, 748, 699.



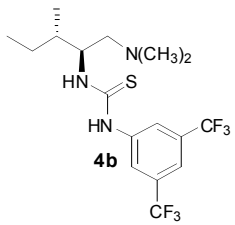
3g

(*S*)–N^1–isopropyl–N^{1,3}–dimethylbutane–1,2–diamine (3g). This compound was obtained from aminoamide **2g** (142 mg, 0.8 mmol) by the method described for **3a**: 120 mg (0.8 mmol, 92% yield). Yellow liquid. **[α]$_D^{25}$**=+43.3 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.87 (d, *J*=6.8 Hz, 6H), 0.91–0.96 (m, 6H), 1.43–1.54 (m, 1H), 1.65 (br s, 2H), 2.06–2.19 (m, 1H), 2.12 (s, 3H), 2.26 (dd, *J*=12.3, 3.4 Hz, 1H), 2.53–2.59 (m, 1H), 2.72–2.81 (m, 1H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 17.1 (CH_3), 18.0 (CH_3), 18.4 (CH_3), 19.4 (CH_3), 32.0 (CH), 37.0 (CH_3), 53.6 (CH), 54.1 (CH), 57.6 (CH_2); **IR** (film) ν 3294, 2963, 1466, 1363, 1152.



4a

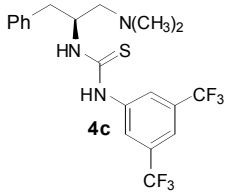
(*S*)–1–(3,5–bis(trifluoromethyl)phenyl)–3–(1–(dimethylamino)–3–methylbutan–2–yl)thiourea (4a). To a solution of the diamine **3a** (325 mg, 2.5 mmol) in dry CH_2Cl_2 (2 mL) was added 3,5–bis(trifluoromethyl)phenyl isothiocyanate (0.47 mL, 2.5 mmol) at 0 °C under argon. The resulting solution was stirred for overnight at room temperature. The reaction was concentrated *in vacuo* and the residue was purified by flash chromatography (chloroform/ethanol = 30:1 to 8:1) to afford a slight yellow solid in 71% yield (711 mg, 1.8 mmol). White solid. **[α]$_D^{25}$**=–27.3 (*c*=1.0, $CHCl_3$); **m.p.** (hexane)=109–110 ºC; **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.03 (d, J=6.9 Hz, 6H), 1.95 (m, 1H), 2.43 (s, 6H), 2.43–2.52 (m, 1H), 2.67–2.75 (m, 1H), 3.56 (m, 1H), 6.27 (br s, 1H), 7.59 (s, 1H), 8.02 (s, 2H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 18.1 (2 CH_3), 31.4 (CH), 45.0 (2 CH_3), 59.8 (CH), 63.9 (CH_2), 117.3 (CH), 122.6 (2 CH), 123.1 (2 CF_3, q, *J*=272.5 Hz), 131.5 (2 C, q, *J*=33.2 Hz), 142.2 (C), 182.7 (C); **^{19}F–NMR** ($CDCl_3$) δ –110.71; **IR** (KBr) ν 3276, 3193, 1551, 1469, 1386, 1286, 1181, 1131; **Anal.** Calcd. for $C_{16}H_{21}F_6N_3S$: C, 47.87; H, 5.27; N, 10.47. Found: C, 48.02; H, 5.10; N, 10.04.



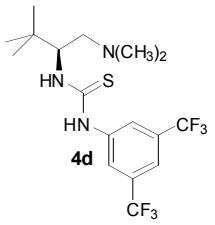
4b

(2*S*,3*S*)-1–(3,5–bis(trifluoromethyl)phenyl)–3–(–1–(dimethylamino)–3–methylpentan–2–yl)thiourea (4b). This compound was obtained from diamine **3b** (87 mg, 0.6 mmol) by the method described for **4a** and purified by flash chromatography (chloroform/ethanol = 30/1): 178

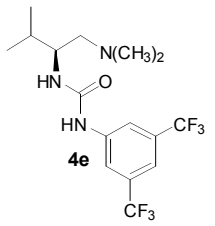
mg (0.4 mmol, 71% yield). White solid. $[\alpha]_D^{25}$=–18.4 (*c*=1.0, $CHCl_3$); **m.p.** (hexane)=85–86 ºC; **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.97 (t, *J*=7.4 Hz, 3H), 0.99 (d, *J*=7.5 Hz, 3H), 1.19–1.36 (m, 1H), 1.39–1.50 (m, 1H), 1.68 (br s, 1H), 2.33–2.51 (m, 1H), 2.43 (s, 6H), 2.67–2.74 (m, 1H), 3.64 (br s, 1H), 6.31 (br s, 1H), 7.59 (s, 1H), 8.02 (s, 2H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 11.7 (CH_3), 14.6 (CH_3), 25.8 (CH_2), 38.6 (CH), 45.1 (2 CH_3), 58.7 (CH), 63.4 (CH_2), 117.4 (CH), 122.6 (2 CH), 123.1 (2 CF_3, q, *J*=272.7 Hz), 131.5 (2 C, q, *J*=33.2 Hz), 142.1 (C), 182.8 (C); **^{19}F–NMR** ($CDCl_3$) δ –110.70; **IR** (KBr) ν 3198, 2966, 1566, 1524, 1382, 1276, 1172; **Anal.** Calcd. for $C_{17}H_{23}F_6N_3S$: C, 49.15; H, 5.58; N, 10.11. Found: C, 49.37; H, 5.26; N, 9.58.



(*S*)–1–(3,5–bis(trifluoromethyl)phenyl)–3–(1–(dimethylamino)–3–phenylpropan–2–yl)thiourea (4c). This compound was obtained from diamine **3c** (323 mg, 1.8 mmol) by the method described for **4a** and purified by flash chromatography (chloroform/ethanol = 60/1): 599 mg (1.3 mmol, 74% yield). Yellow oil. $[\alpha]_D^{25}$=–17.6 (*c*=1.1, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$, 330K) δ 2.31 (s, 6H), 2.49 (dd, J=13.2, 2.2 Hz, 1H), 2.68 (dd, J=13.2, 9.2 Hz, 1H), 2.81 (dd, J=13.8, 8.2 Hz, 1H), 3.06 (dd, J=13.8, 5.7 Hz, 1H), 4.19 (br s, 1H), 6.55 (br s, 1H), 7.21–7.38 (m, 5H), 7.61 (s, 1H), 8.00 (s, 2H); **^{13}C–NMR** (75 MHz, $CDCl_3$, 330K) δ 39.5 (CH_2), 45.1 (2 CH_3), 55.4 (CH), 64.0 (CH_2), 117.8 (CH), 122.8 (2 CH), 123.2 (2 CF_3, q, *J*=272.7 Hz), 127.2 (CH), 128.9 (2 CH), 129.2 (2 CH), 132.2 (2 C, q, *J*=33.5 Hz), 136.5 (C), 141.5 (C), 182.2 (C); **^{19}F–NMR** ($CDCl_3$) δ –110.71; **IR** (film) ν 3246, 1542, 1498, 1474, 1388, 1279, 1180, 1135; **Anal.** Calcd. for $C_{20}H_{21}F_6N_3S$: C, 53.45; H, 4.71; N, 9.35. Found: C, 53.31; H, 4.61; N, 9.22.

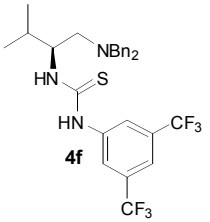


(*S*)–1–(3,5–bis(trifluoromethyl)phenyl)–3–(1–(dimethylamino)–3,3–dimethylbutan–2–yl)thiourea (4d). This compound was obtained from diamine **3d** (146 mg, 1.0 mmol) by the method described for **4a** and purified by flash chromatography (chloroform/ethanol = 30/1 to 8/1): 263 mg (0.6 mmol, 64% yield). White solid. $[\alpha]_D^{25}$=–32.4 (*c*=1.0, $CHCl_3$); **m.p.** (hexane)=121–122 ºC; **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.05 (s 9H), 2.44 (s, 6H), 2.58–2.71 (m, 2H), 3.36–3.41 (m, 1H), 6.26 (d, *J*=4.3 Hz, 1H), 7.57 (s, 1H), 8.03 (s, 2H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 26.4 (3 CH_3), 33.4 (C), 45.0 (2 CH_3), 63.1 (CH_2), 63.8 (CH), 117.1 (CH), 122.2 (2 CH), 123.1 (2 CF_3, q, *J*=272.9 Hz), 131.5 (2 C, q, *J*=33.3 Hz), 142.2 (C), 182.9 (C); **^{19}F–NMR** ($CDCl_3$) δ –110.67; **IR** (KBr) ν 3434, 3221, 1543, 1470, 1383, 1277, 1176, 1132; **Anal.** Calcd. for $C_{17}H_{23}F_6N_3S$: C, 49.15; H, 5.58; N, 10.11. Found: C, 49.17; H, 5.17; N, 10.30.



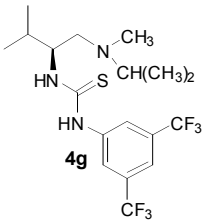
(*S*)–1–(3,5–bis(trifluoromethyl)phenyl)–3–(1–(dimethylamino)–3–methylbutan–2–yl)urea (4e). This compound was obtained from diamine **3a** (300 mg, 2.3 mmol) by the method described for **4a** and purified by flash chromatography (chloroform/ethanol = 30/1 to 8/1): 594 mg (1.5 mmol, 67% yield). White solid. $[\alpha]_D^{25}$=–17.4 (*c*=1.4, $CHCl_3$); **m.p.**

(hexane/EtOAc)=124–126 ºC; **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.98 (d, *J*=7.2 Hz, 3H), 1.00 (d, *J*=7.1 Hz, 3H), 1.84–1.95 (m, 1H), 2.39 (s, 6H), 2.39–2.46 (m, 1H), 2.55–2.62 (m, 1H), 3.55 (br s, 1H), 5.30 (br s, 1H), 7.42 (s, 1H), 7.81 (s, 2H); **^{13}C–NMR** (75 MHz, $CDCl_3$, 330K) δ 17.5 (CH_3), 18.6 (CH_3), 31.2 (CH), 45.4 (2 CH_3), 54.9 (CH), 63.4 (CH_2), 115.1 (CH), 118.4 (2 CH), 123.4 (2 CF_3, q, *J*=272.5 Hz), 132.2 (2 C, q, *J*=33.2 Hz), 141.9 (C), 157.1 (C); **^{19}F–NMR** ($CDCl_3$) δ –110.55; **IR** (KBr) ν 3332, 1660, 1571, 1474, 1389, 1275, 1175, 1140; **Anal.** Calcd. for $C_{16}H_{21}F_6N_3O$: C, 49.87; H, 5.49; N, 10.90. Found: C, 49.79; H, 5.16; N, 10.95.



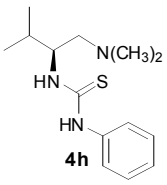
4f

(S)–1–(3,5–bis(trifluoromethyl)phenyl)–3–(1–(dibenzylamino)–3–methylbutan–2–yl)thiourea (4f). This compound was obtained from diamine **3f** (384 mg, 1.3 mmol) by the method described for **4a** and purified by flash chromatography (ethyl acetate/hexane = 20/1 to 5/1): 540 mg (1.0 mmol, 75% yield). Yellow oil. **[α]$_D^{25}$**=0.9 (*c*=0.8, $CHCl_3$); **^{1}H–NMR** (300 MHz, CD_3COCD_3) δ 0.84 (d, *J*=6.6 Hz, 3H), 1.04 (d, *J*=6.6 Hz, 3H), 2.16–2.24 (m, 1H), 2.72 (br d, *J*=7.0 Hz, 2H), 3.01–3.11 (m, 1H), 3.72–3.82 (m, 4H), 5.02 (br s, 1H), 7.31–7.43 (m, 6H), 7.52–7.55 (m, 4H), 7.83 (s, 1H), 8.46 (s, 2H), 9.55 (br s, 1H); **^{13}C–NMR** (75 MHz, CD_3COCD_3) δ 17.3 (CH_3), 19.9 (CH_3), 30.7 (CH), 55.6 (CH_2), 57.5 (CH), 59.3 (2 CH_2), 117.4 (CH), 123.5 (2 CH), 124.4 (2 CF_3, q, *J*=271.0 Hz), 127.8 (2 CH), 129.1 (4 CH), 130.0 (4 CH), 131.8 (2 C, q), 140.4 (2 C), 143. 1 (C), 182.7 (C); **IR** (film) ν 3240, 1654, 1522, 1473, 1382, 1279, 1182, 1137.



4g

(*S*)–1–(3,5–bis(trifluoromethyl)phenyl)–3–(1–(isopropyl(methyl)amino)–3–methylbutan–2–yl)thiourea (4g). This compound was obtained from diamine **3g** (120 mg, 0.8 mmol) by the method described for **4a** and purified by flash chromatography (chloroform/ethanol = 60/1): 206 mg (0.4 mmol, 63% yield). Yellow oil. **[α]$_D^{25}$**=–40.4 (*c*=0.9, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.95–1.28 (m, 12H), 1.90–1.94 (m, 1H), 2.38 (s, 3H), 2.54–2.70 (m, 2H), 2.99 (sp, *J*=6.5 Hz, 1H), 3.59 (br s, 1H), 6.25 (br s, 1H), 7.58 (s, 1H), 8.04 (s, 2H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 16.5 (CH_3), 18.1 (2 CH_3), 18.5 (CH_3), 31.5 (CH), 37.3 (CH_3), 54.3 (CH), 57.9 (CH_2), 60.4 (CH), 117.3 (CH), 122.8 (2 CH), 123.1 (2 CF_3, q, *J*=272.7 Hz), 131.6 (2 C, q, *J*=32.8 Hz), 142.0 (C), 183.3 (C); **IR** (film) ν 3246, 1610, 1473, 1385, 1278, 1178, 1137, 759.

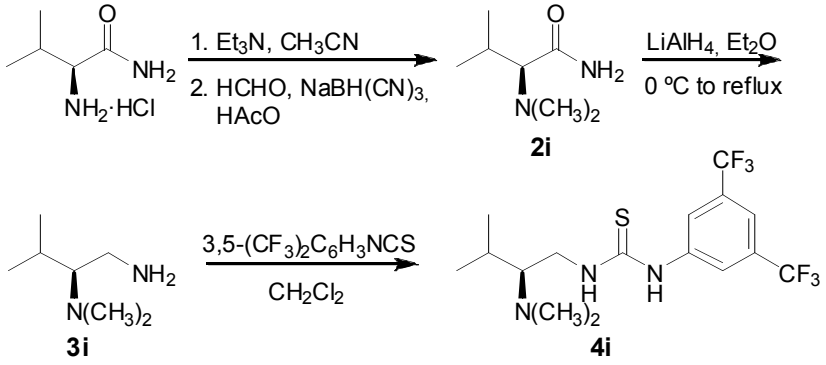


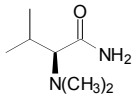
4h

(S)–1–(1–(dimethylamino)–3–methylbutan–2–yl)–3–phenylthiourea (4h). This compound was obtained from diamine **3a** (55 mg, 0.4 mmol) and phenyl isothiocyanate by the method described for **4a** and purified by flash chromatography (chloroform/ethanol = 30/1 to 8/1): 63 mg (0.2 mmol, 57% yield). Yellow oil. **[α]$_D^{25}$**=–60.9 (*c*=0.8, $CHCl_3$); **^{1}H–NMR** (300 MHz, CD_3COCD_3) δ 1.04–1.07 (m, 6H), 2.14–2.30 (m, 1H), 2.39 (s, 6H), 2.34–2.51 (m, 1H), 2.62–2.70 (m, 1H), 3.28 (br s, 1H), 4.62 (br s, 1H), 7.21–7.26 (m, 1H), 7.41–7.46 (m, 2H), 7.62–7.64 (m, 2H); **^{13}C–NMR** (75 MHz, CD_3COCD_3) δ 18.5 (CH_3), 19.0 (CH_3), 31.3 (CH), 45.9 (2 CH_3), 58.4 (CH), 61.1

(CH_2), 124.3 (2 CH), 125.4 (CH), 129.6 (2 CH), 182.5 (C); **IR** (film) ν 3210, 1599, 1534, 1498, 1350, 1309, 1259, 1182.

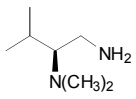
Procedure for preparation of catalyst 4i





2i

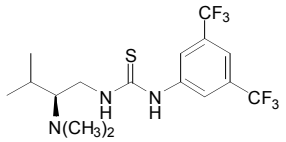
(*S*)–2–(dimethylamino)–3–methylbutanamide (2i).[4] To a suspension of valinamide hydrochloride (157 mg, 1 mmol) in acetonitrile (5.4 mL) was added triethylamine (1 mmol, 0.14 mL) and 40% aqueous formaldehyde (0.4 mL, 5 mmol), and the mixture was stirred for 15 minutes. Sodium cyanoborohydride (132 mg, 2 mmol) was carefully added (exothermic) followed by acetic acid (0.27 mL) 15 minutes later. After 1 hour, the volatiles were removed *in vacuo* and the resulting residue was partitioned between ethyl acetate (5 mL) and 1M NaOH (2.5 mL). The organic layer was washed with 1M NaOH (2×2 mL), brine (2 mL), and dried over $MgSO_4$. The resulting white solid was purified by flash chromatography (ethyl acetate to ethyl acetate/methanol 5/1) to afford the aminoamide **2f** (80 mg, 0.56 mmol, 56%). White solid. $[\alpha]_D^{25}$=–15.6 (*c*=1.0, $CHCl_3$); **m.p.** (hexane/EtOAc)=133–134 ºC; **^{1}H–NMR** (300 MHz, CD_3OD) δ 0.93 (d, *J*=6.6 Hz, 3H), 0.99 (d, *J*=6.7 Hz, 3H), 2.00–2.23 (m, 1H), 2.30 (s, 6H), 2.58 (d, *J*=9.3 Hz, 1H); **^{13}C–NMR** (75 MHz, CD_3OD) δ 19.6 (CH_3), 20.2 (CH_3), 28.2 (CH), 42.3 (2 CH_3), 75.8 (CH), 175.7 (C); **IR** (KBr) ν 3312, 3153, 1670, 1407.



3i

(*S*)–N^2,N^{2,3}–trimethylbutane–1,2–diamine (3i). To a 0 ºC cooled suspension of aminoamide (249 mg, 1.3 mmol) in dry diethyl ether (8 mL) was added LAH in portions (213 mg, 5.3 mmol) under argon. The reaction mixture was refluxed until disappearance of the starting material by TLC (24 hours) and carefully quenched by sequential addition of water (0.21 mL), 15% NaOH (0.21 mL) and water (0.63 mL). The solids were filtered off and washed with diethyl ether, and the filtrate was dried over $MgSO_4$. The solvent was removed in vacuo to afford the diamine **3f**: 120 mg (0.9 mmol, 69%). Yellow liquid. $[\alpha]_D^{25}$=+6.6 (*c*=1.0, $CHCl_3$); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 0.85 (d, *J*=6.8 Hz, 3H), 0.93 (d, *J*=6.8 Hz, 3H), 1.79–1.90 (m, 1H), 2.01 (br s, 2H), 2.01–2.11 (m, 1H), 2.34 (s, 6H), 2.55–2.70 (m, 2H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 19.6 (CH_3), 22.1 (CH_3), 27.0 (CH), 39.2 (CH_2), 41.0 (2 CH_3), 71.6 (CH); **IR** (film) ν 3172, 2960, 1458, 733.

[4] D. E. Fuerst, E. N. Jacobsen. *J. Am. Chem. Soc.*, **2005**, *127*, 8964-8965

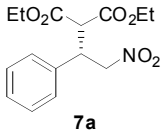


4i

(*S*)–1–(3,5–bis(trifluoromethyl)phenyl)–3–(2–(dimethylamino)–3–methylbutyl)thiourea (4i). This compound was obtained from diamine **3i** (416 mg, 3.2 mmol) by the method described for **4a** and purified by flash chromatography (chloroform/ethanol = 60/1 to 15/1): 620 mg (1.5 mmol, 48% yield). White solid. $[\alpha]_D^{25}$=–5.8 (*c*=0.8, $CHCl_3$); **m.p.** (hexane)=90–92 ºC; **^{1}H–NMR** (300 MHz, $CDCl_3$, 330K) δ 0.95 (d, *J*=6.7 Hz, 3H), 1.03 (d, *J*=6.7 Hz, 3H), 1.95–2.06 (m, 1H), 2.30–2.44 (m, 1H), 2.36 (s, 6H), 3.30 (dd, *J*=13.8, 9.8 Hz, 1H), 3.73 (br s, 1H), 7.67 (s, 1H), 7.79 (s, 2H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 19.3 (CH_3), 22.3 (CH_3), 27.0 (CH), 40.4 (2 CH_3), 43.6 (CH_2), 67.4 (CH), 118.4 (CH), 122.8 (2 CH), 122.8 (2 CF_3, q, *J*=269.2 Hz), 132.7 (2 C, q, *J*=34.6 Hz), 139.2 (C), 178.8 (C); **^{19}F–NMR** ($CDCl_3$) δ –110.68; **IR** (KBr) ν 3157, 1549, 1467, 1382, 1279, 1182, 1134; **Anal.** Calcd. for $C_{16}H_{21}F_6N_3S$: C, 47.87; H, 5.27; N, 10.47. Found: C, 48.16; H, 5.07; N, 10.56.

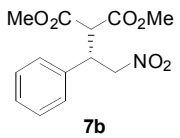
Typical procedure for enantioselective Michael addition of 1,3–dicarbonyl compounds to nitroolefins

To a stirred solution of *trans*–β–nitrostyrene **5a** (0.30 mmol, 45.6 mg) and catalyst **4a** (0.03 mmol) in dry toluene (0.6 mL) was added diethyl malonate **6a** (0.60 mmol, 0.09 mL) at –18 ºC under argon. The reaction mixture was stirred until disappearance of the nitroolefin by TLC. The solvent was removed in vacuo and the residue was purified by flash chromatography (hexane/AcOEt = 20/1 as eluent) to afford desired product **7a**.



7a

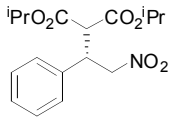
Diethyl (*S*)-2–(nitro–1–phenylethyl)malonate (7a). White solid. $[\alpha]_D^{25}$=+6.8 (*c*=1.0, $CHCl_3$, 95% ee) (lit.[5] $[\alpha]_D^{25}$=–6.00, 93%ee, R); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.05 (t, *J*=7.1 Hz, 3H), 1.26 (t, *J*=7.1 Hz, 3H), 3.82 (d, *J*=9.4 Hz, 1H), 4.01 (q, *J*=7.1 Hz, 2H), 4.19–4.27 (m, 3H), 4.86 (dd, *J*=13.1, 8.9 Hz, 1H), 4.93 (dd, *J*=13.1, 5.2 Hz, 1H), 7.22–7.35 (m, 5H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 13.6 (CH_3), 13.9 (CH_3), 42.9 (CH), 54.9 (CH), 61.8 (CH_2), 62.0 (CH_2), 77.6 (CH_2), 127.9 (2 CH), 128.2 (CH), 128.8 (2 CH), 136.2 (C), 166.7 (C), 167.4 (C); **HPLC** (Chiralpak AS–H, hexane/isopropanol = 90:10, 1.0 mL/min, λ=220 nm); t_R=11.8 min (major, S), 13.5 min (minor, R). **HRMS** calcd for $C_{15}H_{19}NO_6 + Na^+$, 332.1110; found, 332.1100.



7b

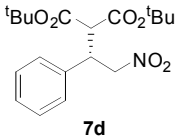
(*S*)–Dimethyl 2–(2–nitro–1–phenylethyl)malonate (7b). White solid. $[\alpha]_D^{25}$=+4.8 (*c*=1.2, $CHCl_3$, 93% ee) (lit.[5] $[\alpha]_D^{25}$=–6.15, 89% ee, R); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 3.57 (s, 3H), 3.77 (s, 3H), 3.87 (d, *J*=9.0 Hz, 1H), 4.26 (td, *J*=8.8, 5.6 Hz, 1H), 4.88 (dd, *J*=13.2, 8.5 Hz, 1H), 4.94 (dd, *J*=13.2, 5.5 Hz, 1H), 7.22–7.36 (m, 5H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 42.8 (CH), 52.7 (CH_3), 52.9 (CH_3), 54.6 (CH), 77.3 (CH_2), 127.8 (2 CH), 128.3 (CH), 128.9 (2 CH), 136.1 (C), 167.2 (C), 167.8 (C); **HPLC** (Chiralpak AD, hexane/isopropanol = 90:10, 1.0 mL/min, λ=220 nm); t_R=18.5 min (minor, R), 24.3 min (major, S). **HRMS** calcd for $C_{13}H_{15}NO_6 + Na^+$, 304.0797; found, 304.0804.

[5] T. Okino, Y. Hoashi, T. Furukawa, X. Xu, Y. Takemoto. *J. Am. Chem. Soc.* **2005**, *127*, 119-125



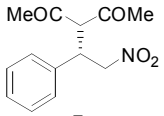
7c

(*S*)–Diisopropyl 2–(2–nitro–1–phenylethyl)malonate (7c). White solid. $[\alpha]_D^{25}$=+8.3 (*c*=0.7, $CHCl_3$, 91% ee) (lit.[5] $[\alpha]_D^{25}$=–7.18, 88% ee, R); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.02 (d, *J*=6.3 Hz, 3H), 1.07 (d, *J*=6.3 Hz, 3H), 1.25 (d, *J*=6.3 Hz, 6H), 3.76 (d, *J*=9.6 Hz, 1H), 4.21 (td, *J*=9.4, 4.8 Hz, 1H), 4.83 (sp, *J*=6.3 Hz, 1H), 4.84 (dd, *J*=12.9, 9.3 Hz, 1H), 4.93 (dd, *J*=13.0, 4.8 Hz, 1H), 5.09 (sp, *J*=6.3 Hz, 1H), 7.22–7.34 (m, 5H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 21.2 (2 CH_3), 21.4 (CH_3), 21.5 (CH_3), 42.9 (CH), 55.1 (CH), 69.4 (CH), 69.8 (CH), 77.9 (CH_2), 128.1 (2 CH), 128.2 (CH), 128.8 (2 CH), 136.3 (C), 166.3 (C), 167.0 (C); **HPLC** (Chiralcel OD, hexane/isopropanol = 95:5, 1.0 mL/min, λ=254 nm); t_R=9.5 min (minor, R), 11.5 min (major, S). **HRMS** calcd for $C_{17}H_{23}NO_6$ + Na^+, 360.1423; found, 360.1405.



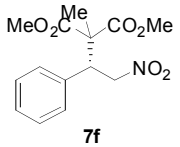
7d

Di–*tert*–butyl 2–(2–nitro–1–phenylethyl)malonate (7d). White solid. **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.23 (s, 9H), 1.47 (s, 9H), 3.62 (d, *J*=9.8 Hz, 1H), 4.13 (td, *J*=9.7, 4.4 Hz, 1H), 4.80 (dd, *J*=12.7, 9.7 Hz, 1H), 4.94 (dd, *J*=12.8, 4.4 Hz, 1H), 7.22–7.34 (m, 5H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 27.4 (3 CH_3), 27.8 (3 CH_3), 43.0 (CH), 56.4 (CH), 78.2 (CH_2), 82.2 (C), 82.8 (C), 128.1 (CH), 128.3 (2 CH), 128.7 (2 CH), 136.5 (C), 166.0 (C), 166.8 (C); **HPLC** (Chiralcel OD, hexane/isopropanol = 90:10, 1.0 mL/min, λ=220 nm); t_R=5.8 min, 6.5 min.



7e

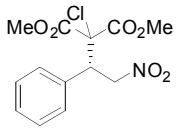
(*S*)–3–(2–nitro–1–phenylethyl)pentane–2,4–dione (7e). White solid. $[\alpha]_D^{25}$=+113.6 (*c*=1.0, $CHCl_3$, 93% ee) (lit.[6] $[\alpha]_D^{25}$=–147.6, 95% ee, R); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.93 (s, 3H), 2.28 (s, 3H), 4.20–4.28 (m, 1H), 4.37 (d, *J*=10.7 Hz, 1H), 4.62–4.69 (m, 2H), 7.17–7.20 (m, 2H), 7.26–7.35 (m, 3H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 29.6 (CH_3), 30.4 (CH_3), 42.7 (CH), 70.5 (CH), 78.0 (CH_2), 127.8 (2 CH), 128.4 (CH), 129.2 (2 CH), 135.9 (C), 201.0 (C), 201.7 (C); **HPLC** (Chiralpak AS–H, hexane/isopropanol = 80:20, 1.0 mL/min, λ=210 nm); t_R=10.9 min (major, S), 15.6 min (minor, R). **HRMS** calcd for $C_{13}H_{15}NO_4$ + Na^+, 272.0899; found, 272.0902.



7f

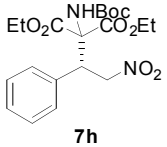
(*R*)–Dimethyl 2–methyl–2–(2–nitro–1–phenylethyl)malonate (7f). White solid. $[\alpha]_D^{25}$=–40.2 (*c*=0.7, $CHCl_3$, 95% ee) (lit.[5] $[\alpha]_D^{25}$=+32.3, 93% ee); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.36 (s, 3H), 3.74 (s, 3H), 3.78 (s, 3H), 4.18 (dd, *J*=9.3, 5.2 Hz, 1H), 5.04–5.07 (m, 2H), 7.15–7.18 (m, 2H), 7.27–7.32 (m, 3H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 20.2 (CH_3), 48.3 (CH), 52.8 (CH_3), 53.0 (CH_3), 56.7 (C), 77.4 (CH_2), 128.4 (CH), 128.7 (2 CH), 128.9 (2 CH), 134.9 (C), 170.7 (C), 171.3 (C); **HPLC** (Chiralpak OD, hexane/isopropanol = 90:10, 1.0 mL/min, λ=220 nm); t_R=10.3 min (major), 21.0 min (minor). **HRMS** calcd for $C_{14}H_{17}NO_6$ + Na^+, 318.0954; found, 318.0944.

[6] J. Wang, H. Li, W. Duan, L. Zu, W. Wang. *Org. Lett.* **2005**, *7*, 4713-4716



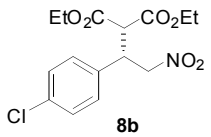
7g

(*S*)–Dimethyl 2–chloro–2–(2–nitro–1–phenylethyl)malonate (7g). White solid. $[\alpha]_D^{25}$=+4.6 (*c*=0.9, $CHCl_3$, >99% ee) (lit.[5] $[\alpha]_D^{25}$=–6.16, 99% ee); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 3.61 (s, 3H), 3.86 (s, 3H), 4.65 (dd, *J*=10.3, 3.5 Hz, 1H), 5.01 (dd, *J*=13.6, 10.3 Hz, 1H), 5.23 (dd, *J*=13.6, 3.5 Hz, 1H), 7.22–7.41 (m, 5H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 48.3 (CH), 54.0 (CH_3), 54.2 (CH_3), 71.7 (C), 76.7 (CH_2), 128.7 (2 CH), 128.9 (CH), 129.1 (2 CH), 133.2 (C), 164.8 (C), 166.5 (C); **HPLC** (Chiralcel OD, hexane/isopropanol = 90:10, 1.0 mL/min, λ=220 nm); t_R=11.3 min (major), 18.1 min (minor). **HRMS** calcd for $C_{13}H_{14}ClNO_6$ + Na^+, 338.0407; found, 338.0403.



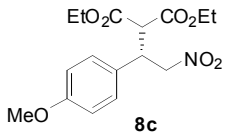
7h

(*S*)–Diethyl 2–(tert–butoxycarbonylamino)–2–(2–nitro–1–phenylethyl)malonate (7h). White solid. $[\alpha]_D^{25}$=–33.7 (*c*=0.6, $CHCl_3$, 79% ee) (lit.[5] $[\alpha]_D^{25}$=+27.1, 82% ee); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.20 (t, *J*=7.2 Hz, 3H), 1.26 (t, *J*=7.1 Hz, 3H), 1.44 (s, 9H), 3.96–4.02 (m, 1H), 4.08–4.17 (m, 1H), 4.19–4.34 (m, 2H), 4.59–4.75 (m, 2H), 5.49 (dd, *J*=12.6, 2.7 Hz, 1H), 5.92 (s, 1H), 7.20–7.30 (m, 5H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 13.8 (CH_3), 13.9 (CH_3), 28.1 (3 CH_3), 48.2 (CH), 62.7 (CH_2), 63.4 (CH_2), 67.5 (C), 77.0 (CH_2), 81.2 (C), 128.6 (2 CH), 128.7 (CH), 128.9 (2 CH), 134.0 (C), 154.7 (C), 166.2 (C), 166.3 (C); **HPLC** (Chiralpak AD, hexane/isopropanol = 90:10, 1.0 mL/min, λ=220 nm); t_R=5.5 min (major), 7.0 min (minor). **HRMS** calcd for $C_{20}H_{28}N_2NaO_8$ + Na^+, 447.1743; found, 447.1721.



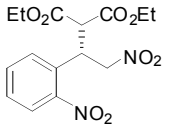
8b

Diethyl (*S*)-2–(1–(4–chlorophenyl)–2–nitroethyl)malonate (8b). White solid. $[\alpha]_D^{25}$=+8.6 (*c*=1.0, $CHCl_3$, 93% ee) (lit.[5] $[\alpha]_D^{25}$=–8.56, >99%ee, R); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.09 (t, *J*=7.3 Hz, 3H), 1.26 (t, *J*=7.1 Hz, 3H), 3.78 (d, *J*=9.3 Hz, 1H), 4.03 (q, *J*=7.2 Hz, 2H), 4.18–4.27 (m, 3H), 4.83 (dd, *J*=13.2, 9.2 Hz, 1H), 4.92 (dd, *J*=13.2, 5.0 Hz, 1H), 7.19 (d, *J*=8.6 Hz, 2H), 7.30 (d, *J*=8.5 Hz, 2H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 13.7 (CH_3), 13.9 (CH_3), 42.3 (CH), 54.6 (CH), 62.0 (CH_2), 62.2 (CH_2), 77.3 (CH_2), 129.1 (2 CH), 129.4 (2 CH), 134.2 (C), 134.7 (C), 166.6 (C), 167.2 (C); **HPLC** (Chiralpak AS–H, hexane/isopropanol = 90:10, 1.0 mL/min, λ=220 nm); t_R=12.6 min (major, S), 14.1 min (minor, R). **HRMS** calcd for $C_{15}H_{18}ClNO_6$ + Na^+, 366.0720; found, 366.0723.



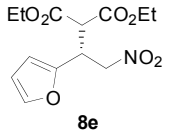
8c

(*S*)-Diethyl 2–(1–(4–methoxyphenyl)–2–nitroethyl)malonate (8c). White solid. $[\alpha]_D^{25}$=+6.2 (*c*=1.3, $CHCl_3$, 94% ee) (lit.[5] $[\alpha]_D^{25}$=–5.87, 91%ee); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.07 (t, *J*=7.2 Hz, 3H), 1.26 (t, *J*=7.1 Hz, 3H), 3.76 (s, 3H), 3.78 (d, *J*=10.0 Hz, 1H), 4.01 (q, *J*=7.1 Hz, 2H), 4.14–4.26 (m, 3H), 4.81 (dd, *J*=13.0, 9.2 Hz, 1H), 4.89 (dd, *J*=12.9, 5.0 Hz, 1H), 6.83 (d, *J*=8.7 Hz, 2H), 7.16 (d, *J*=8.7 Hz, 2H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 13.7 (CH_3), 13.8 (CH_3), 42.2 (CH), 55.0 (CH), 55.1 (CH_3), 61.7 (CH_2), 62.0 (CH_2), 77.8 (CH_2), 114.1 (2 CH), 127.9 (C), 129.1 (2 CH), 159.3 (C), 166.8 (C), 167.4 (C); **HPLC** (Chiralpak AD, hexane/isopropanol = 60:40, 1.0 mL/min, λ=220 nm); t_R=8.9 min (minor), 20.6 min (major). **HRMS** calcd for $C_{16}H_{21}NO_7$ + Na^+, 362.1216; found, 362.1212.



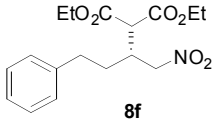
8d

(*S*)–Diethyl 2–(2–nitro–1–(2–nitrophenyl)ethyl)malonate (8d). Yellow oil. $[\alpha]_D^{25}$=+1.6 (*c*=0.8, $CHCl_3$, 87% ee); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.11 (t, *J*=7.1 Hz, 3H), 1.26 (t, *J*=7.2 Hz, 3H), 4.08 (q, *J*=7.2 Hz, 2H), 4.18–4.29 (m, 3H), 4.75 (td, *J*=8.1, 4.3 Hz, 1H), 5.05 (dd, *J*=13.9, 4.3 Hz, 1H), 5.17 (dd, *J*=13.7, 7.9 Hz, 1H), 7.42–7.46 (m, 1H), 7.50 (dd, *J*=7.8, 1.7 Hz, 1H), 7.59 (td, *J*=7.6, 1.4 Hz, 1H), 7.94 (dd, *J*=8.1, 1.4 Hz, 1H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 13.6 (CH_3), 13.8 (CH_3), 37.5 (CH), 53.6 (CH), 62.2 (CH_2), 62.3 (CH_2), 76.2 (CH_2), 125.4 (CH), 129.0 (CH), 129.2 (CH), 131.2 (C), 133.3 (CH), 149.9 (C), 166.6 (C), 167.2 (C); **Anal.** Calcd. for $C_{15}H_{18}N_2O_8$: C, 50.85; H, 5.12; N, 7.91. Found: C, 50.80; H, 4.96; N, 7.60; **HPLC** (Chiralpak AS–H, hexane/isopropanol = 95:5, 1.0 mL/min, λ=220 nm); t_R=30.6 min (minor), 32.7 min (major). **HRMS** calcd for $C_{15}H_{18}N_2O_8$ + Na^+, 377.0961; found, 337.0957.



8e

(*R*)-Diethyl 2–(1–(furan–2–yl)–2–nitroethyl)malonate (8e). Yellow oil. $[\alpha]_D^{25}$=–3.1 (*c*=1.3, $CHCl_3$, 95% ee); (lit.[7] $[\alpha]_D^{25}$=–2.8, 95% ee); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.20 (t, *J*=7.2 Hz, 3H), 1.26 (t, *J*=7.2 Hz, 3H), 3.90 (d, *J*=7.9 Hz, 1H), 4.15 (q, *J*=7.2 Hz, 2H), 4.22 (q, *J*=7.2 Hz, 2H), 4.38 (td, *J*=7.9, 5.4 Hz, 1H), 4.89–4.92 (m, 2H), 6.22 (dd, *J*=2.8, 0.7 Hz, 1H), 6.29 (dd, *J*=3.3, 1.8 Hz, 1H), 7.34–7.35 (m, 1H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 13.8 (CH_3), 13.8 (CH_3), 36.7 (CH), 52.9 (CH), 62.1 (2 CH_2), 75.3 (CH_2), 108.3 (CH), 110.4 (CH), 142.6 (CH), 149.5 (C), 166.7 (C); 167.0 (C); **HPLC** (Chiralcel OD, hexane/isopropanol = 60:40, 1.0 mL/min, λ=254 nm); t_R=5.6 min (major), 8.0 min (minor). **HRMS** calcd for $C_{13}H_{17}NO_7$ + Na^+, 322.0903; found, 322.0895.



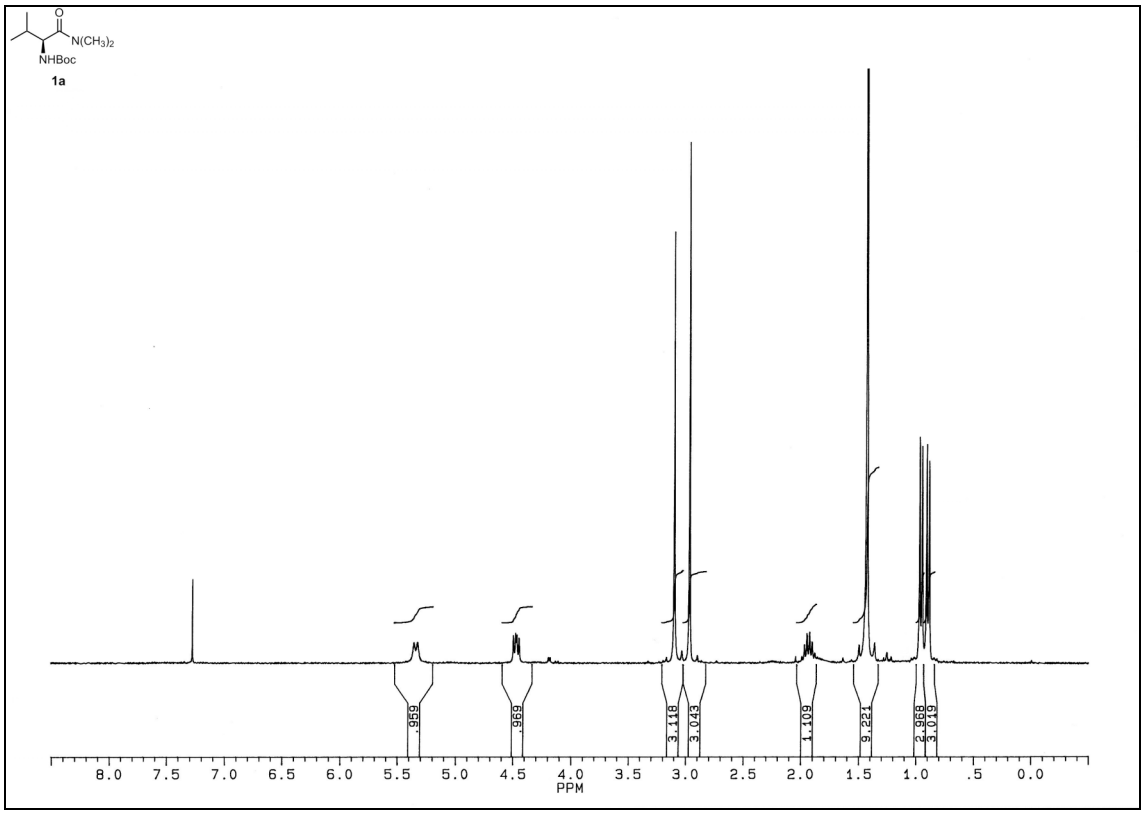
8f

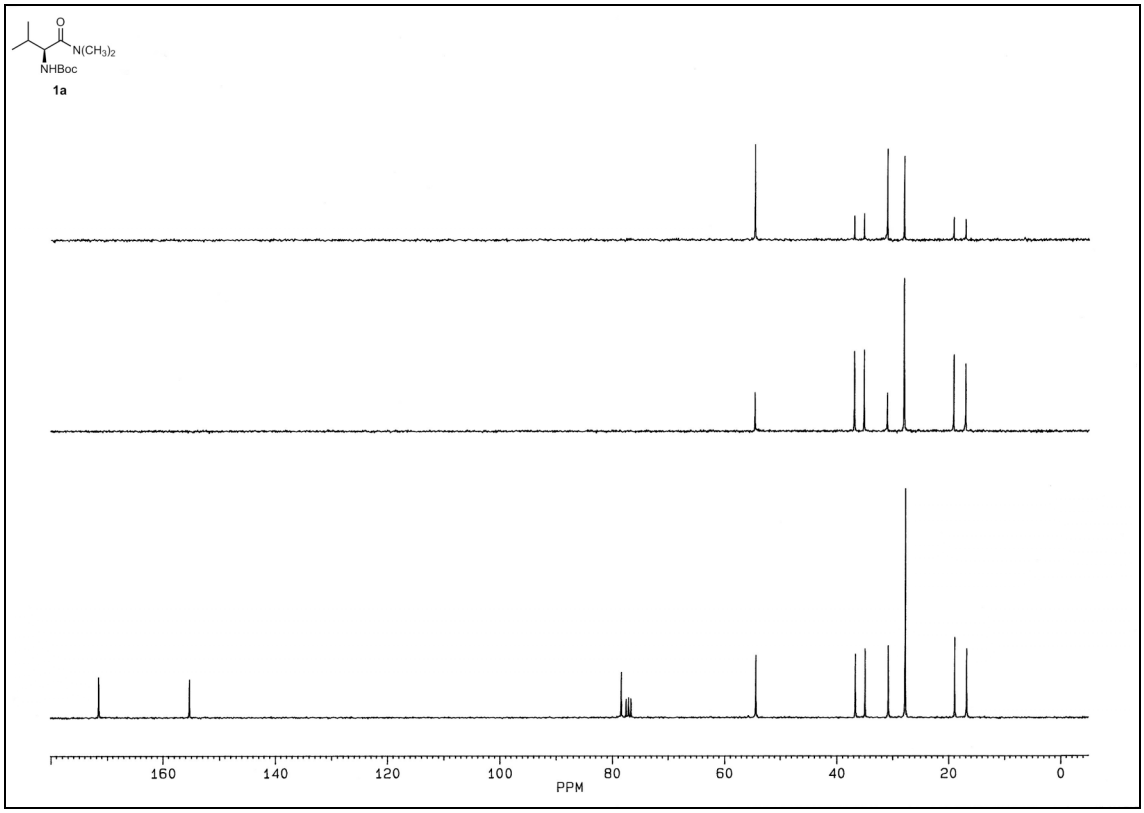
(R)–Diethyl 2–(1–nitro–4–phenylbutan–2–yl)malonate (8f). Colorless oil. $[\alpha]_D^{25}$=–1.0 (*c*=1.2, $CHCl_3$, 81% ee); **^{1}H–NMR** (300 MHz, $CDCl_3$) δ 1.26–1.33 (m, 6H), 1.79–1.87 (m, 2H), 2.69–2.74 (m, 2H), 2.91–3.01 (m, 1H), 3.68 (d, *J*=5.9 Hz, 1H), 4.18–4.31 (m, 4H), 4.59 (dd, *J*=13.4, 6.8 Hz, 1H), 4.76 (dd, *J*=13.4, 5.0 Hz, 1H), 7.16–7.33 (m, 5H); **^{13}C–NMR** (75 MHz, $CDCl_3$) δ 14.0 (2 CH_3), 31.8 (CH_2), 32.9 (CH_2), 36.5 (CH), 52.5 (CH), 61.8 (CH_2), 61.9 (CH_2), 76.4 (CH_2), 126.3 (CH), 128.2 (2 CH), 128.5 (2 CH), 140.3 (C), 167.6 (C), 167.8 (C); **HPLC** (Chiralcel OD, hexane/isopropanol = 95:5, 1.0 mL/min, λ=220 nm); t_R=16.1 min (major), 20.1 min (minor).

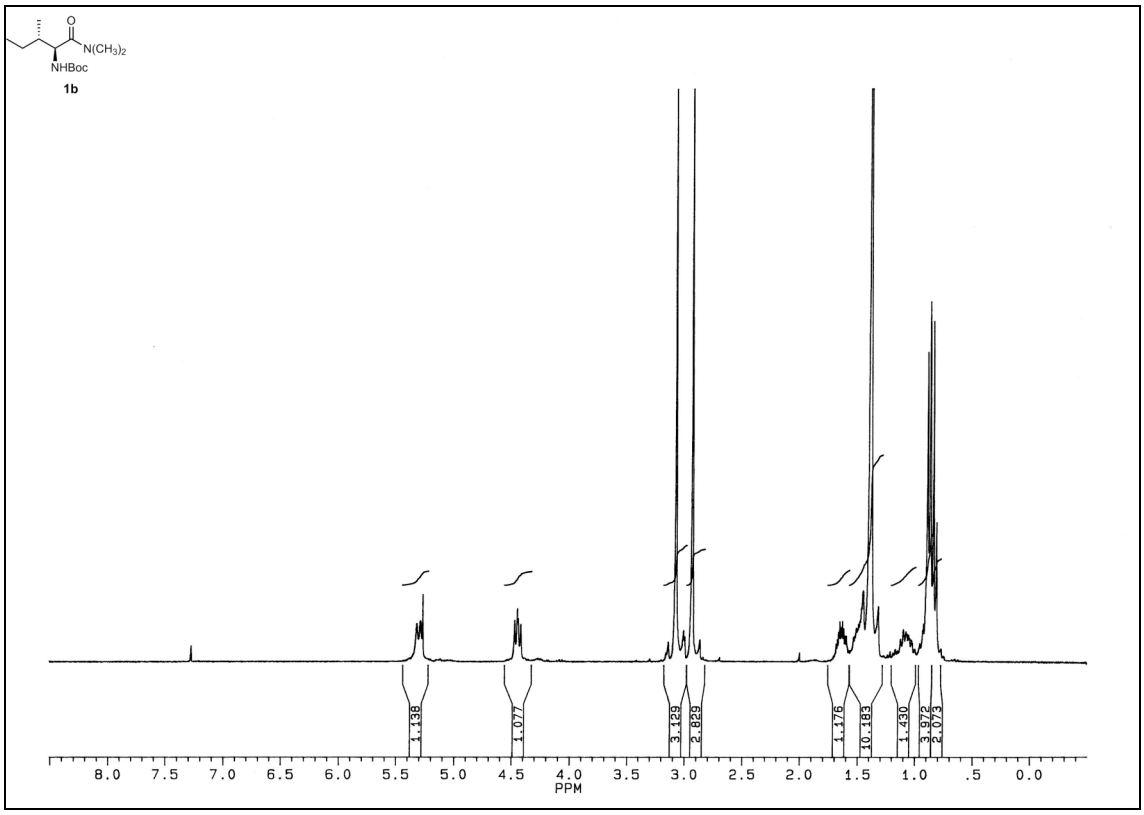
[7] D. A. Evans, S. Mito, D. Seidel. *J. Am. Chem. Soc.* **2007**, *129*, 11583-11592

^{1}H and ^{13}C–NMR spectra

Compounds 1–3



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10.183
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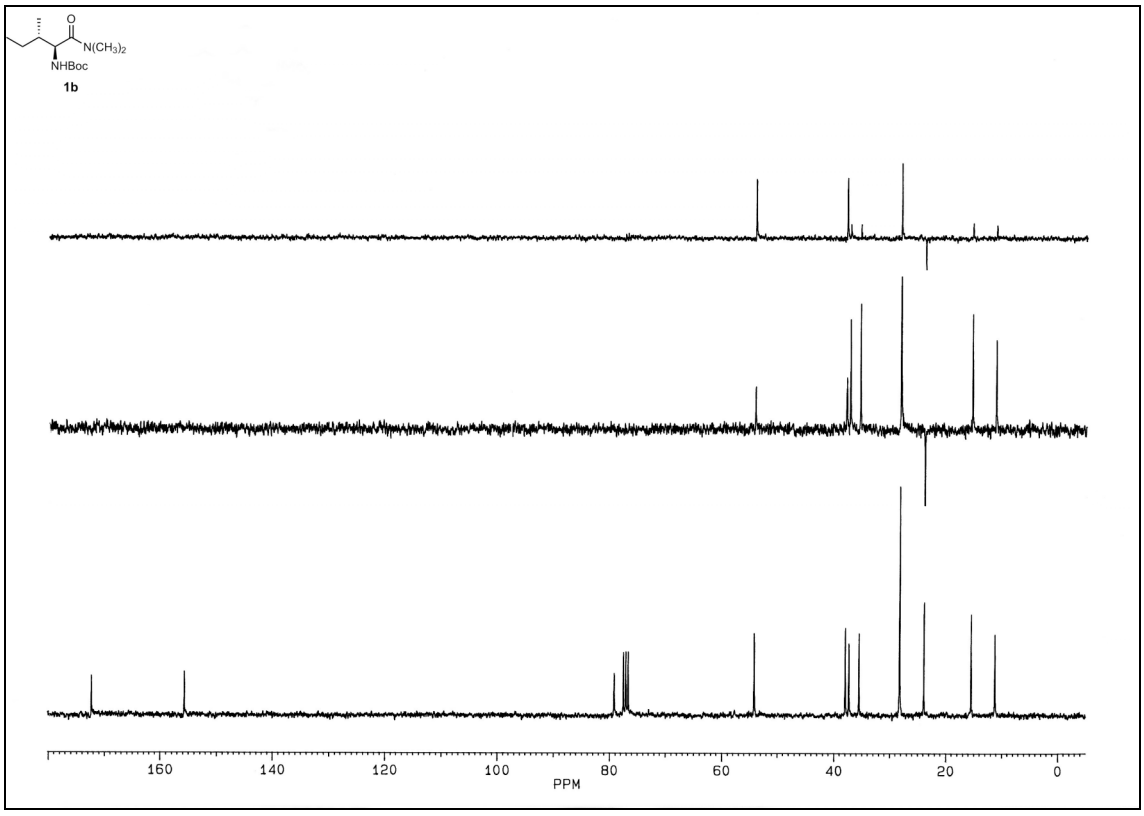
PPM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NHBoc
1b
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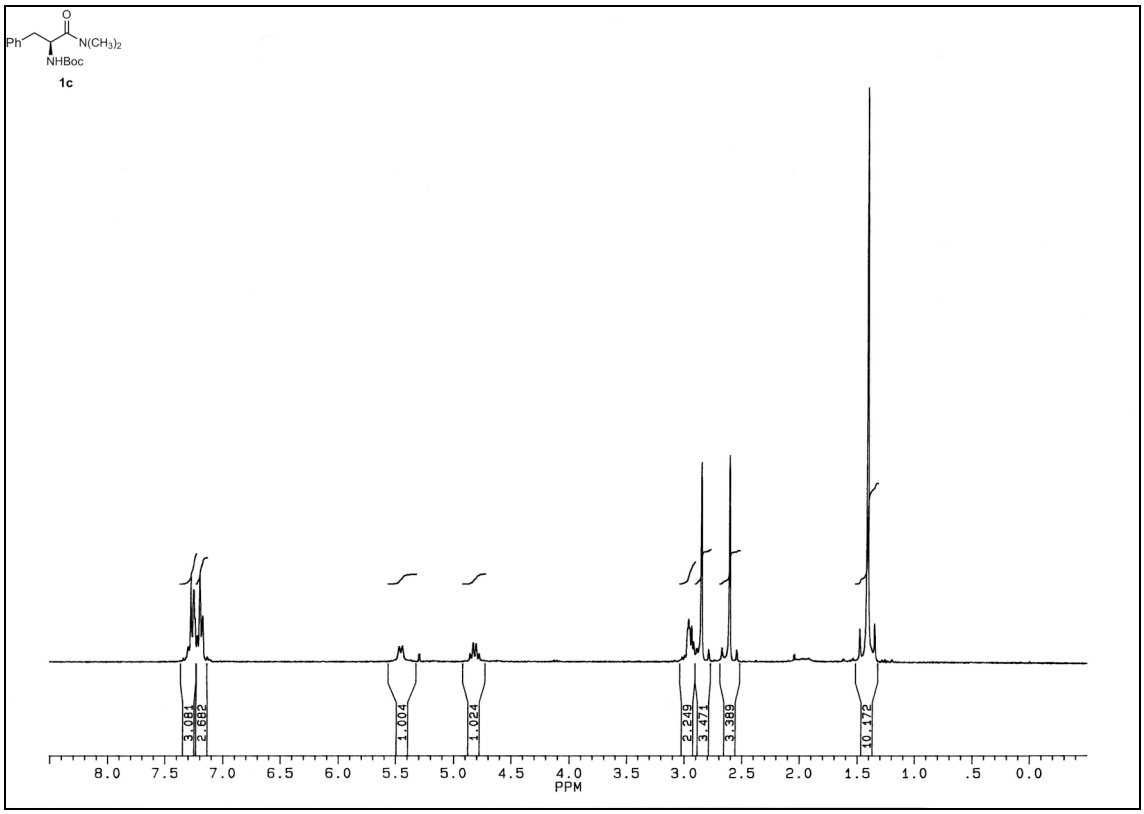
PPM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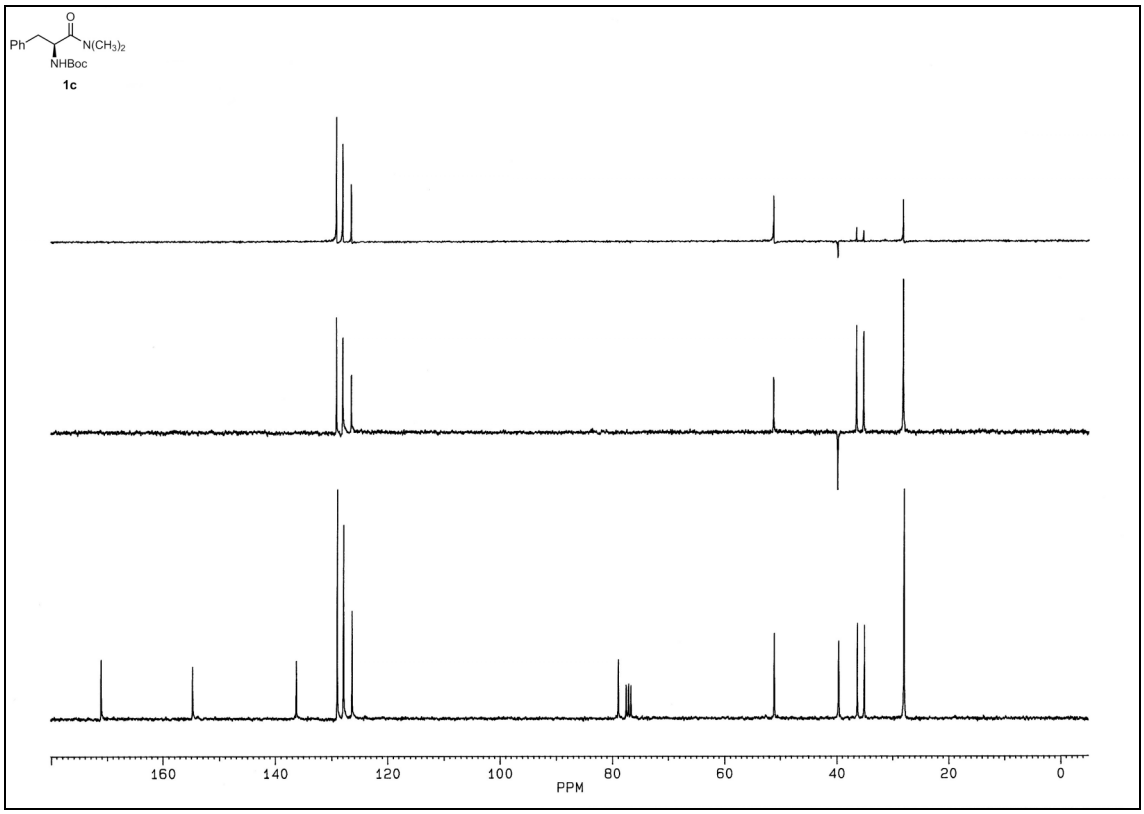
PPM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N(CH3)2
NHBoc
1c
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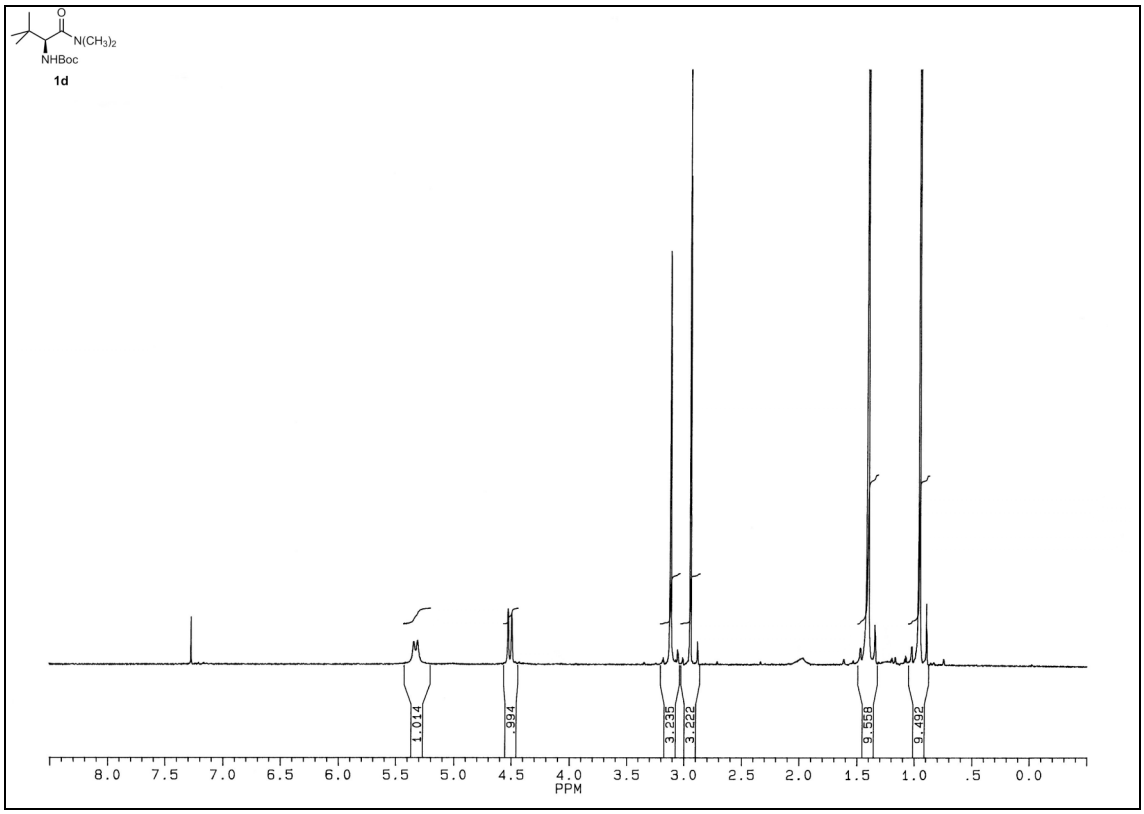
PPM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3.222
9.558
9.492
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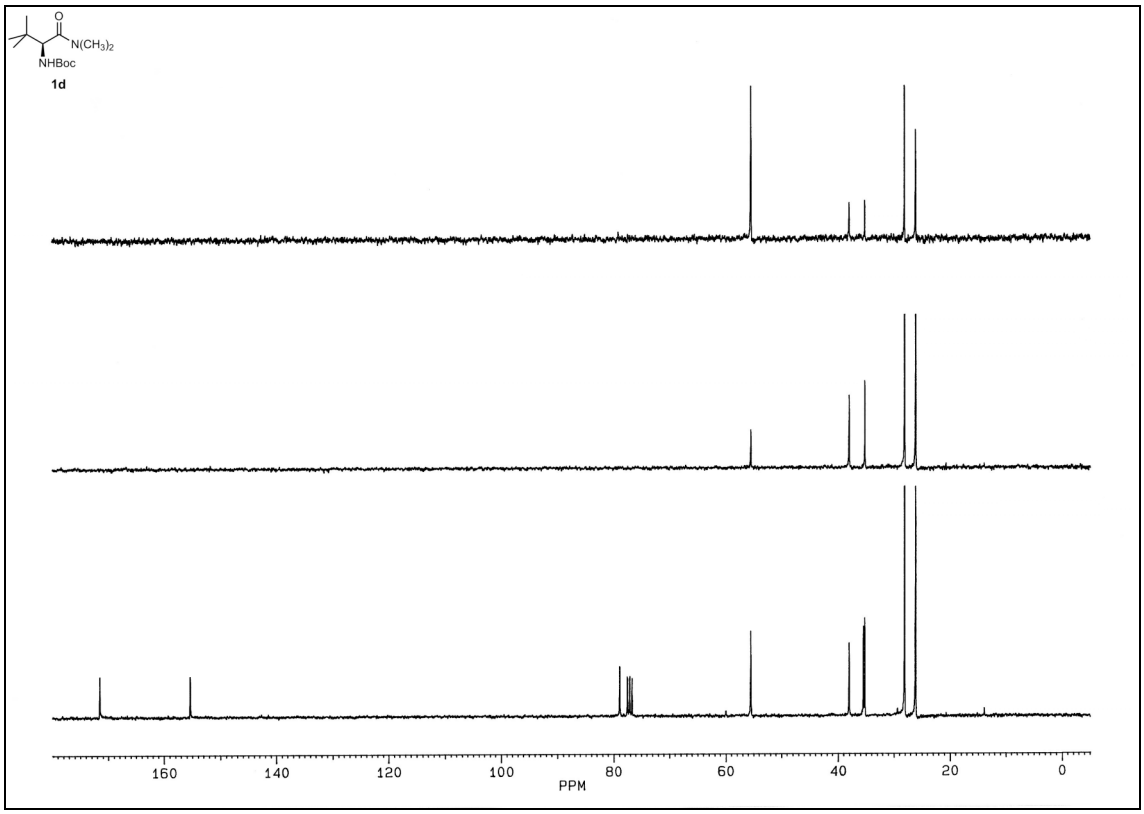
PPM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N(CH3)2
NHBoc
1d
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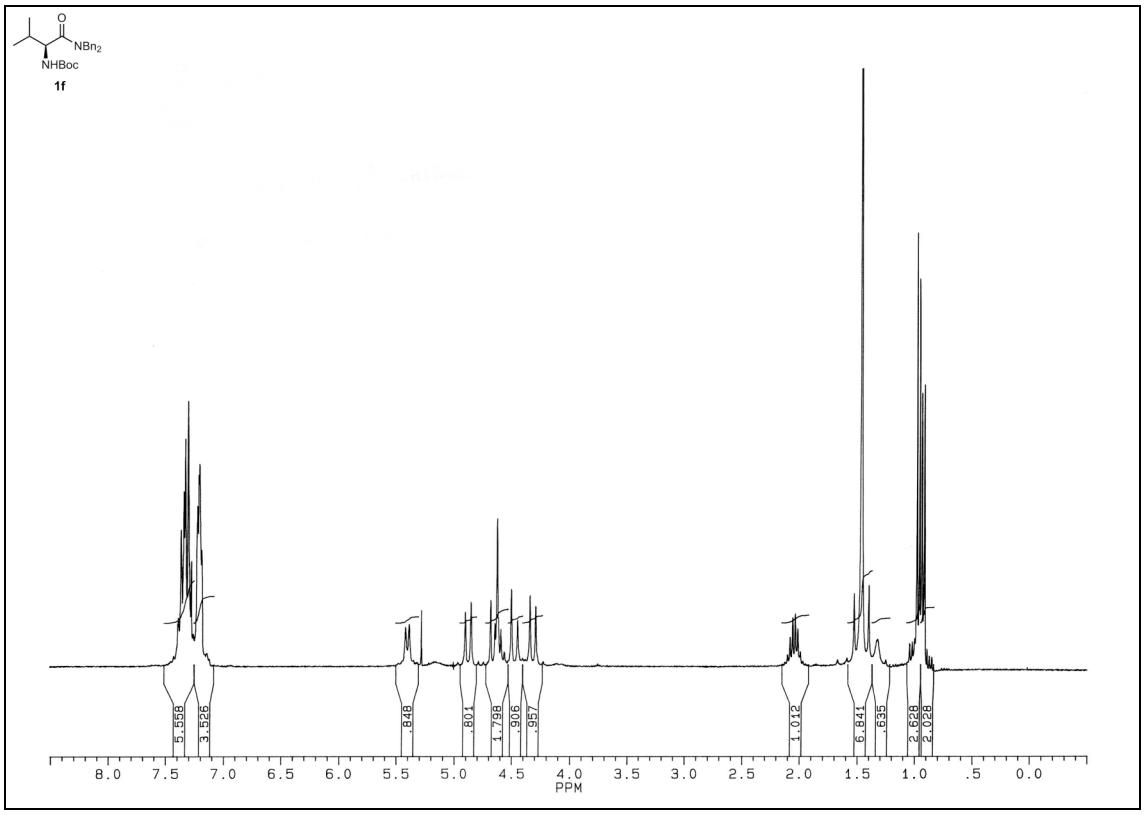
PPM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.635
2.628
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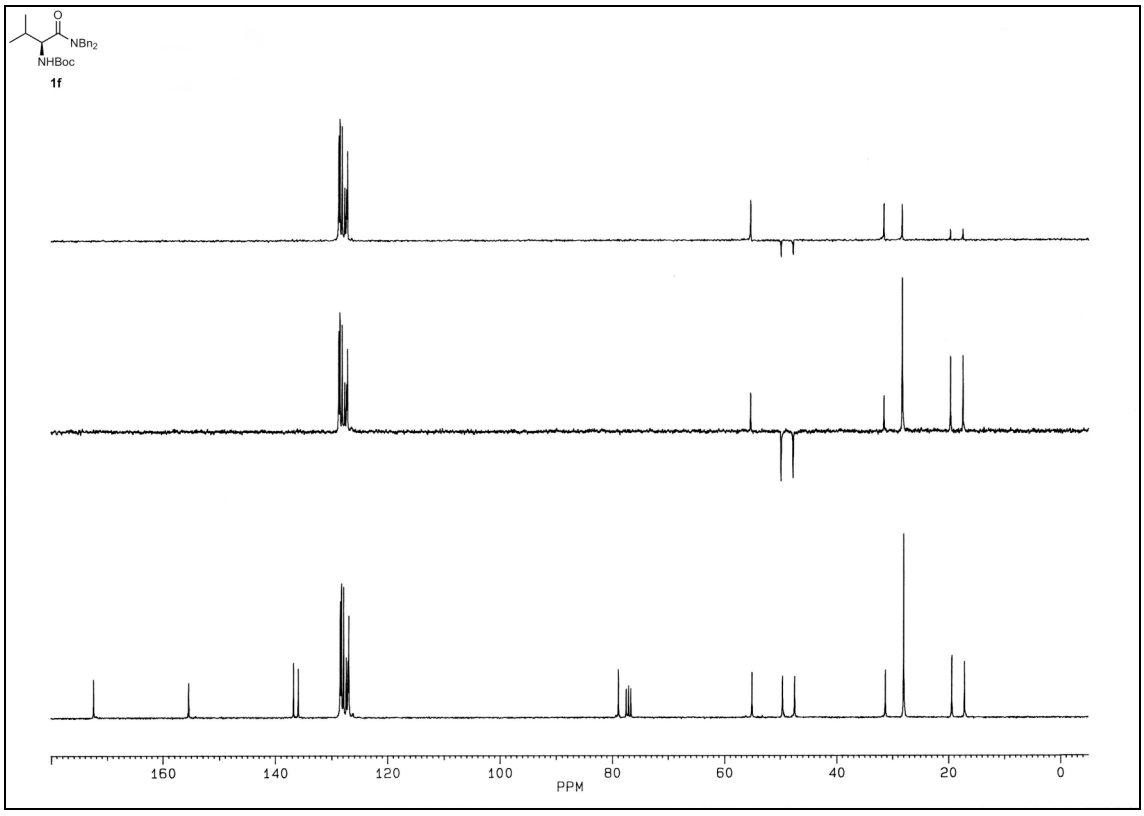
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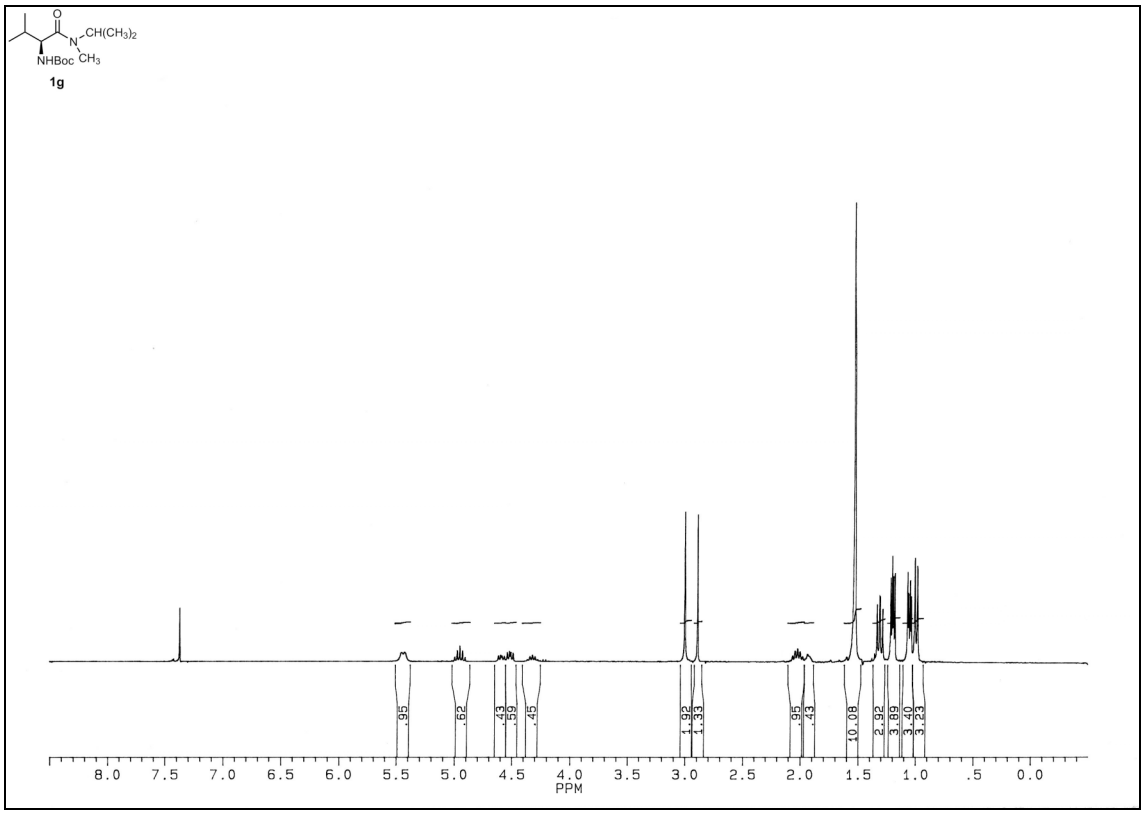
NBn2
NHBoc
1f
160 140 120 100 80 60 40 20 0
PPM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N
CH(CH3)2
NHBoc
CH3
1g
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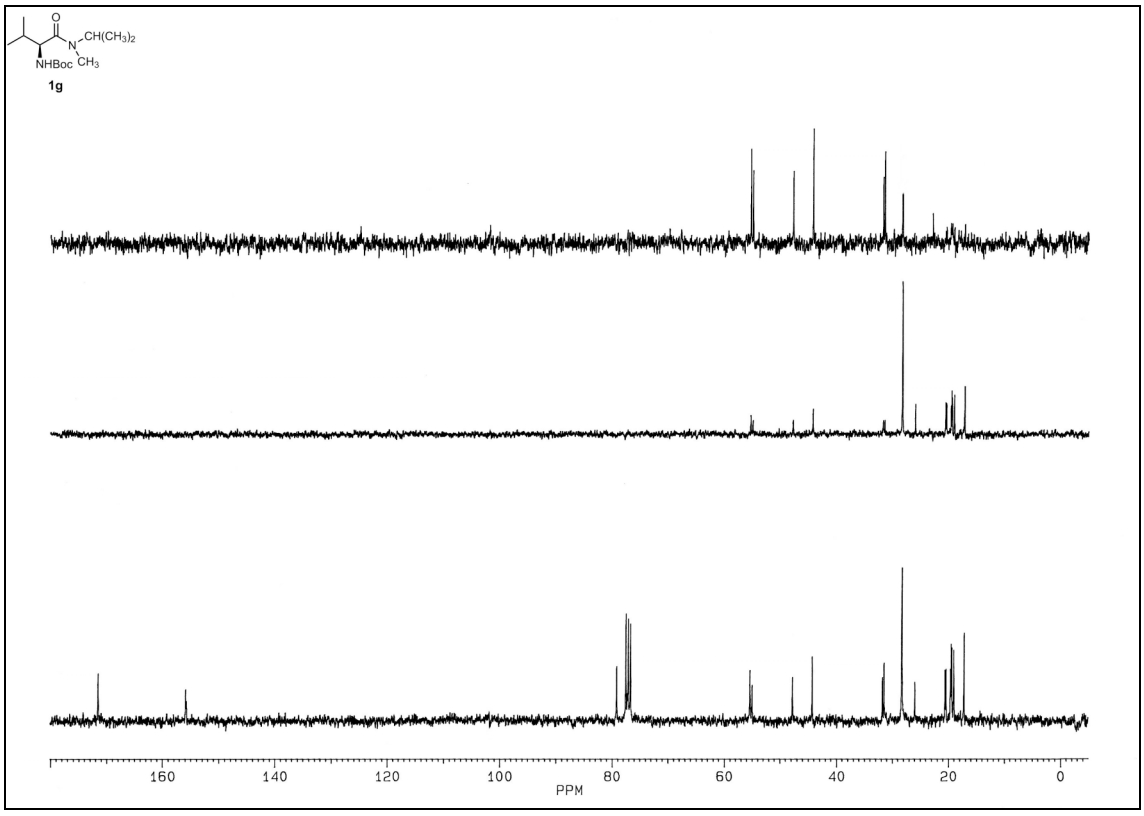
.62
.43
.59
.45
1.92
1.33
.95
.43
10.08
2.92
3.89
3.40
3.23
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
PPM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CH3
1g
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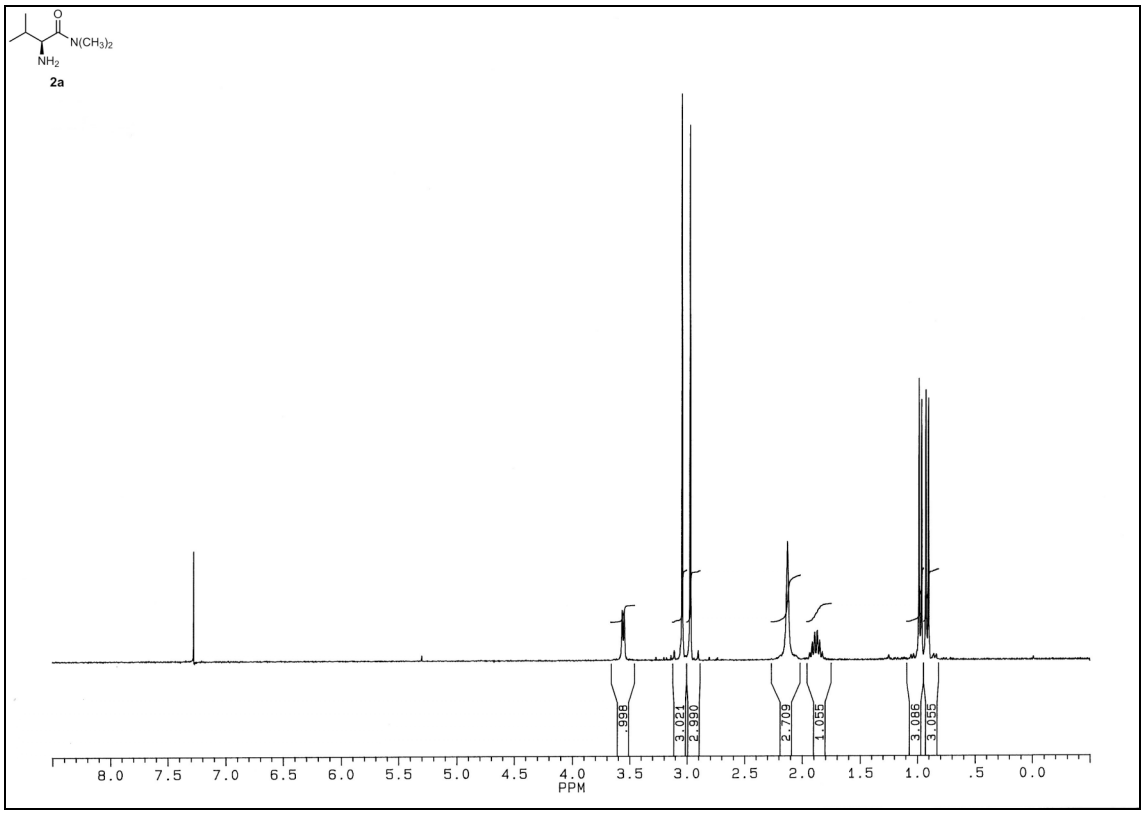
140
120
100
80
60
40
20
0
PPM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3.021
2.990
2.709
1.055
3.086
3.055
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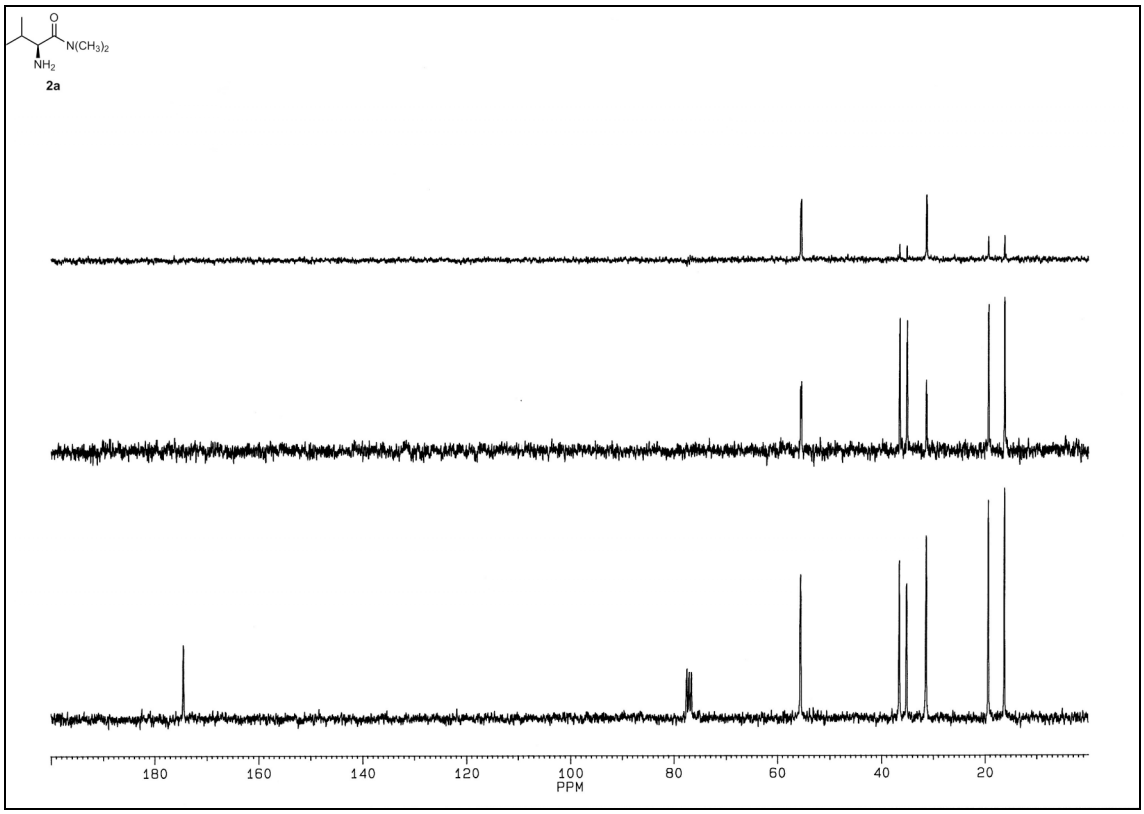
PPM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NH2
2a
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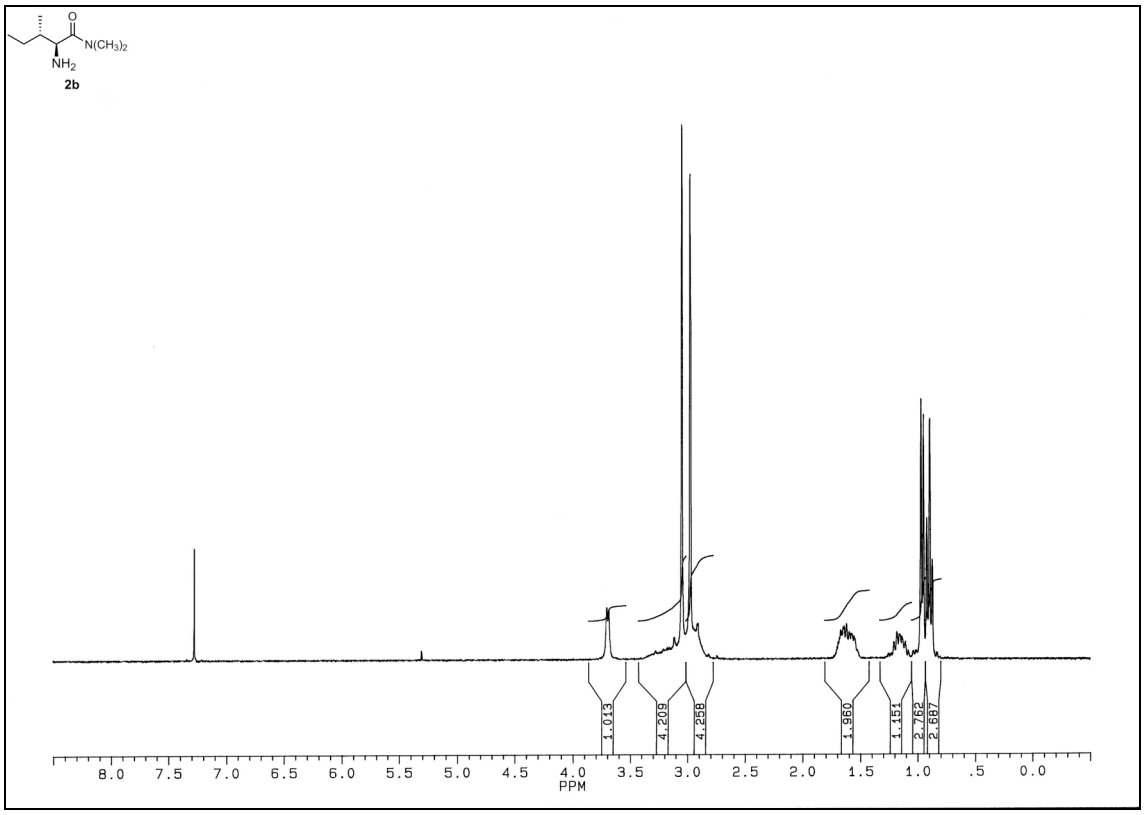
PPM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NH2
2b
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1.960
1.151
2.762
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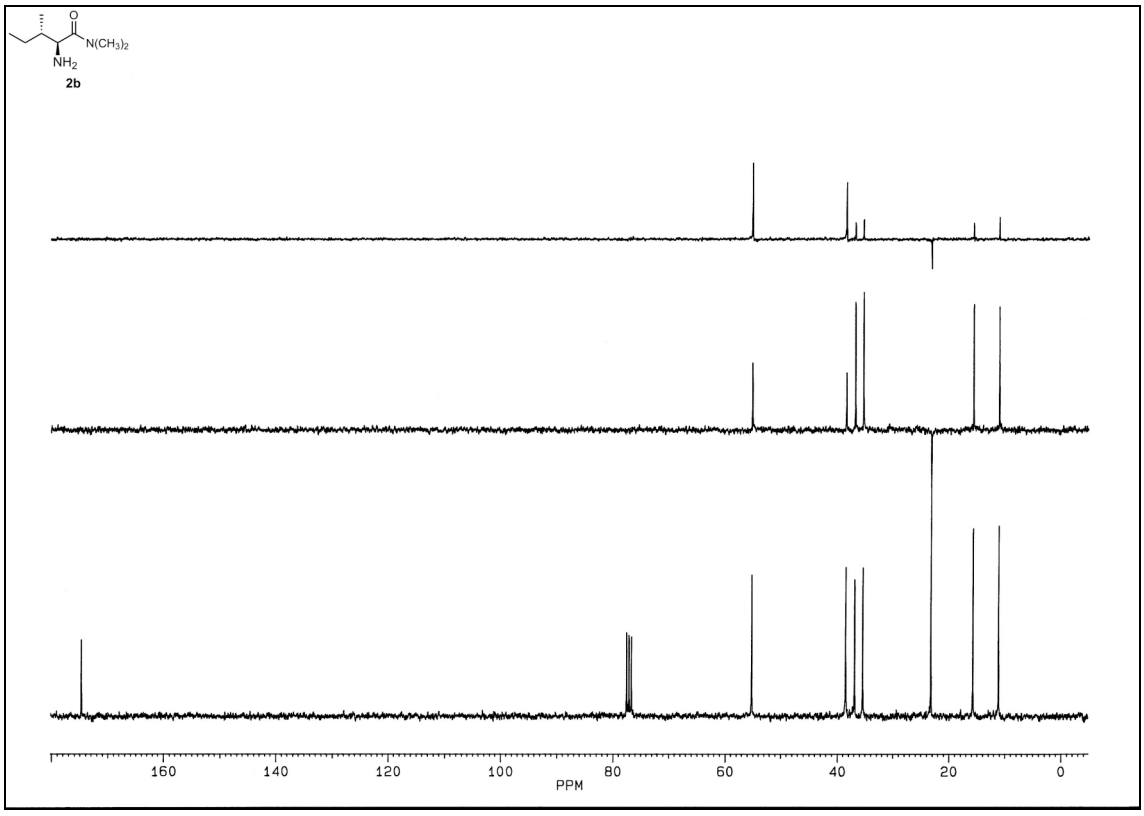
PPM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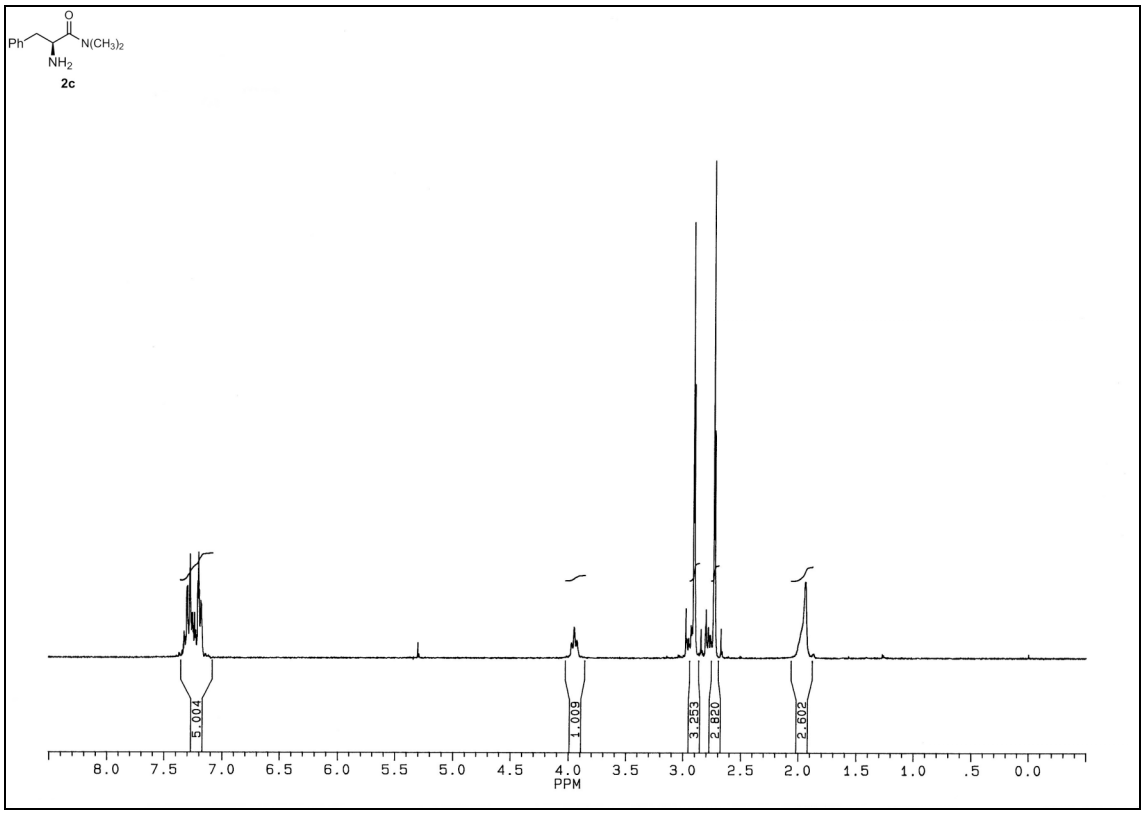
NH2
2b
160 140 120 100 80 60 40 20 0
PPM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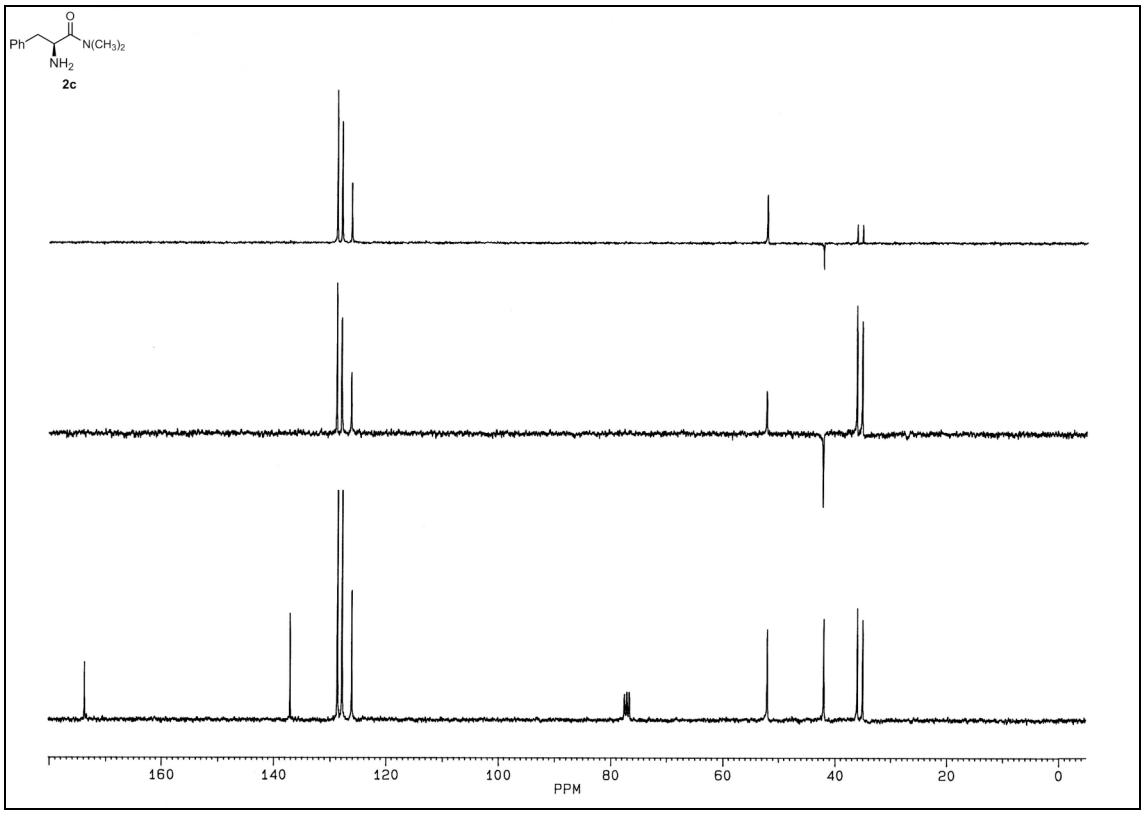
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NH2
2c
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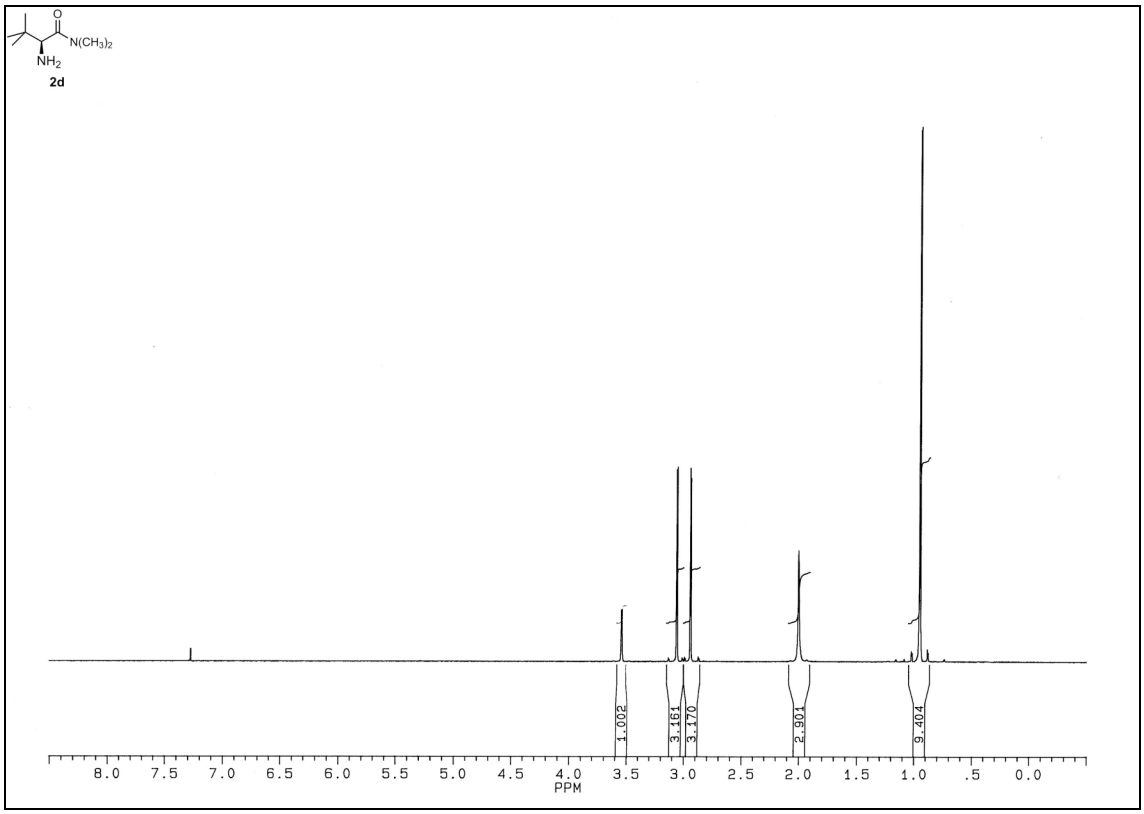
PPM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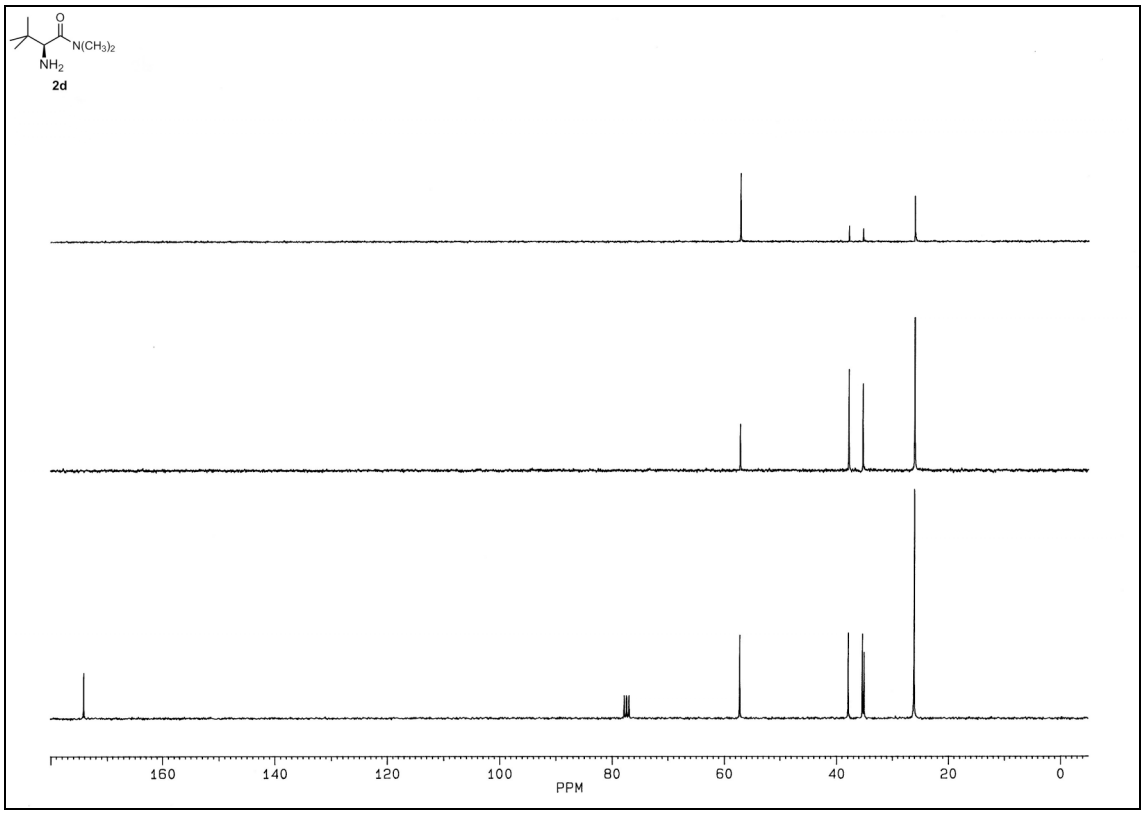
PPM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NH2
2d
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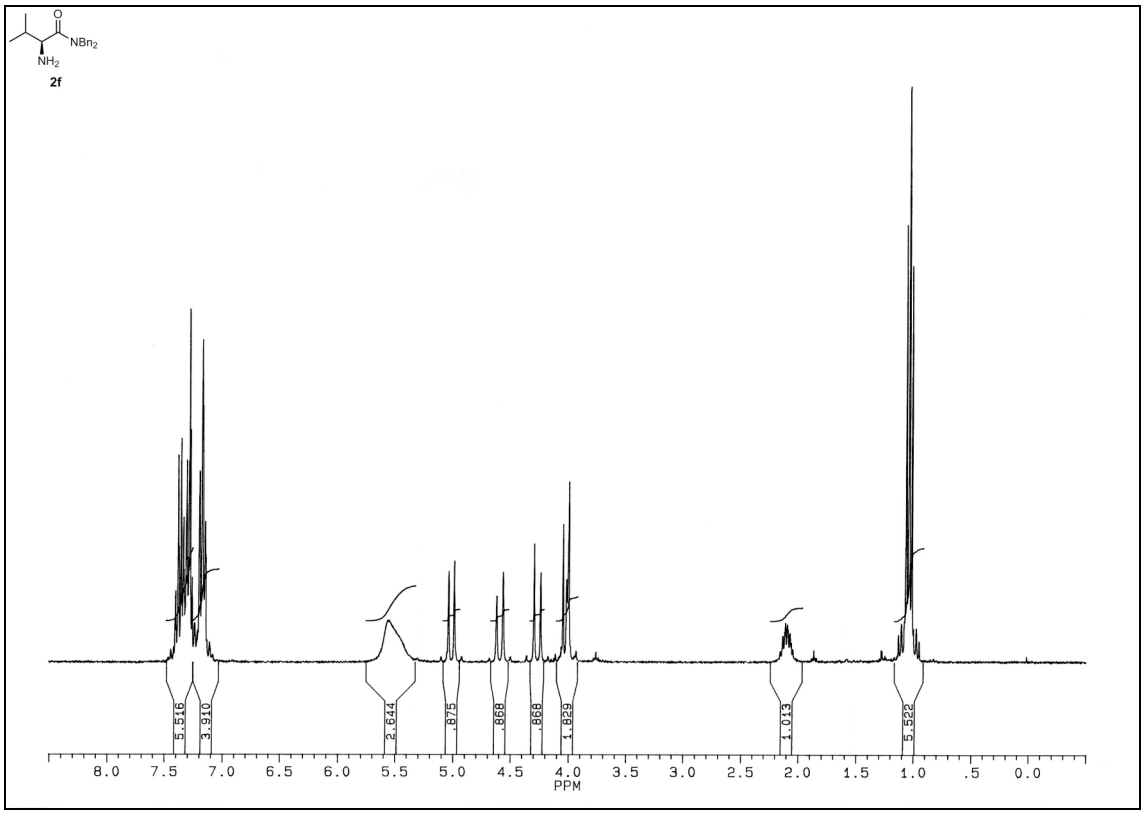
PPM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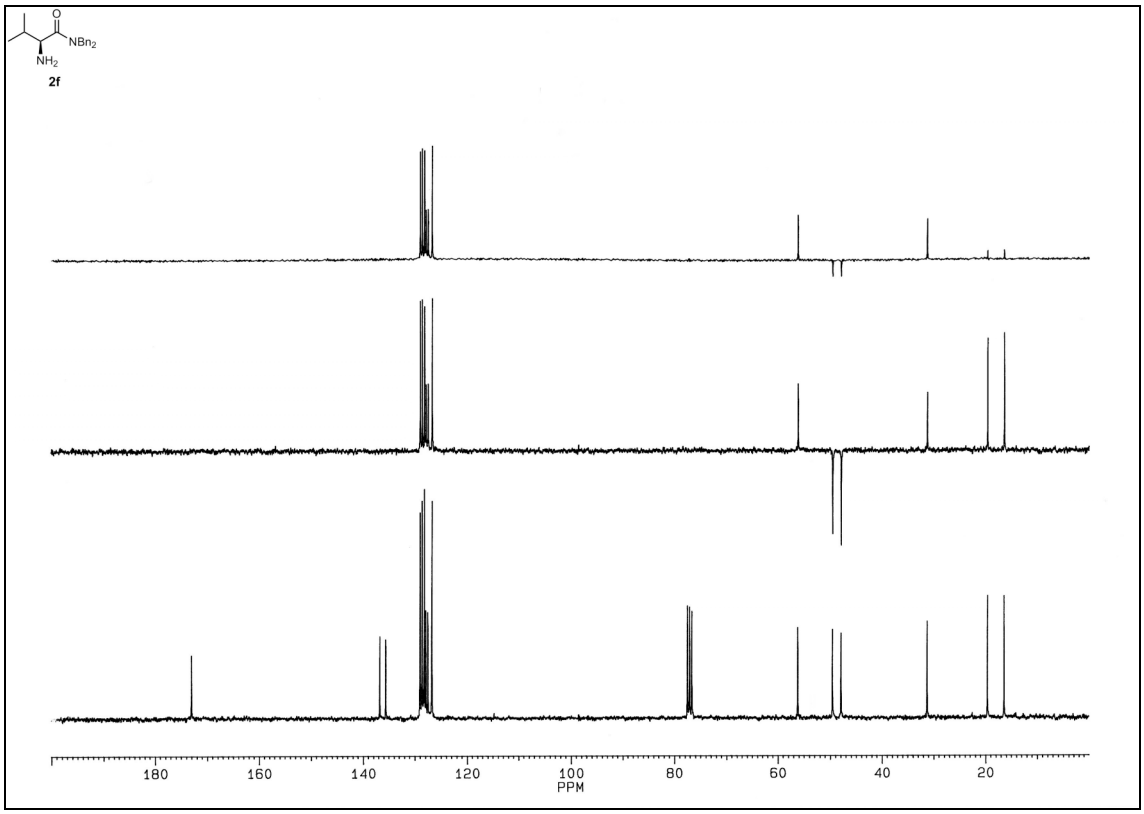
PPM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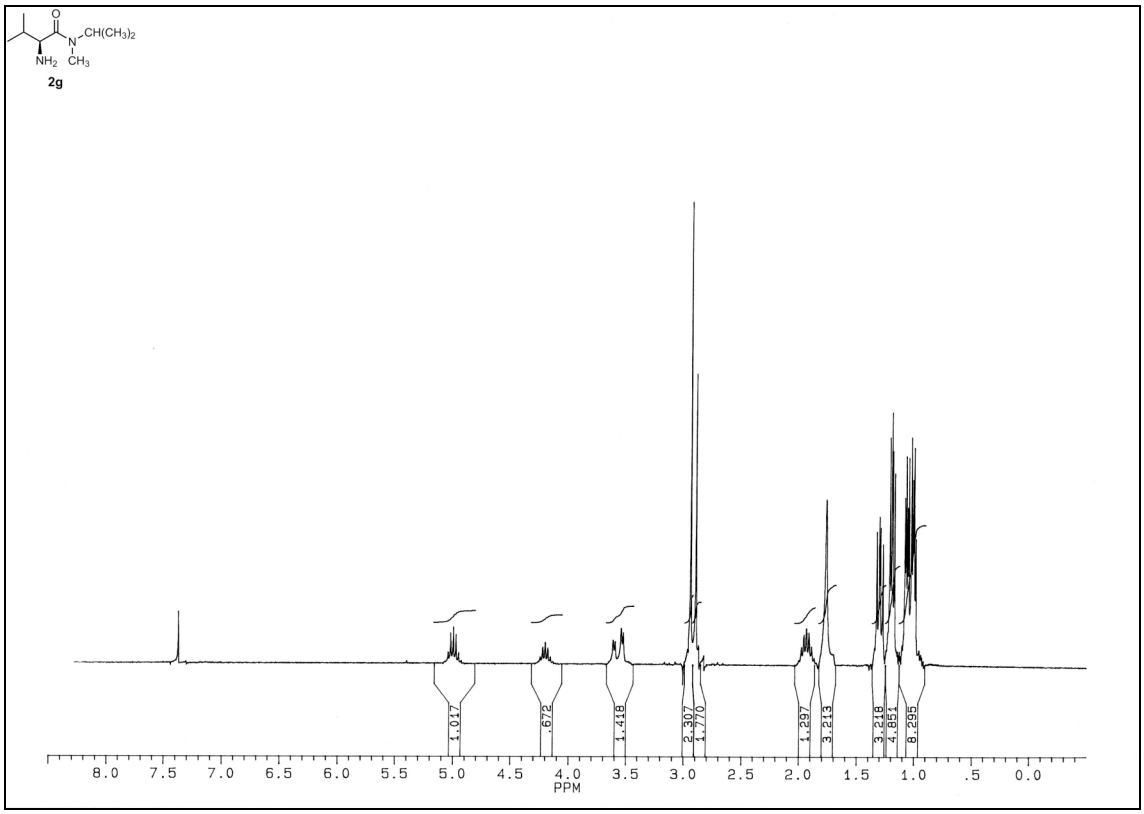
NBn2
NH2
2f
180 160 140 120 100 80 60 40 20
PPM


2g
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1.418
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1.297
3.213
3.218
4.851
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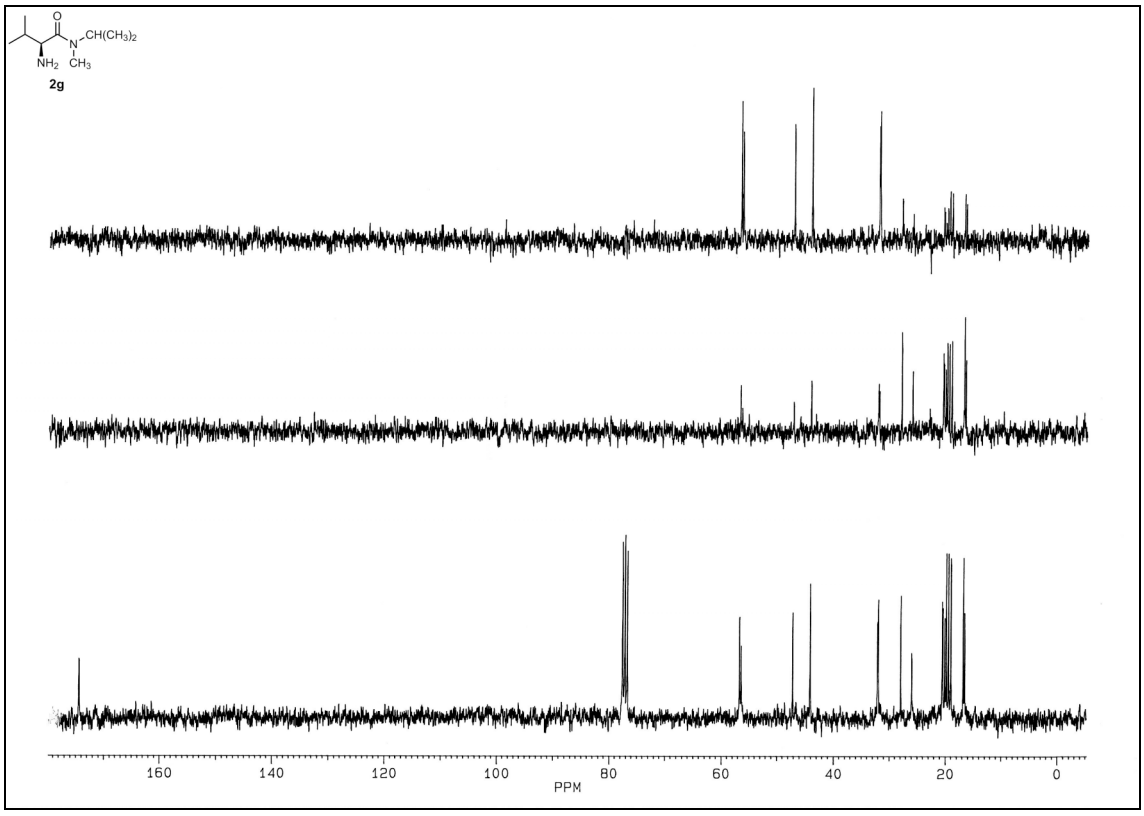
2g
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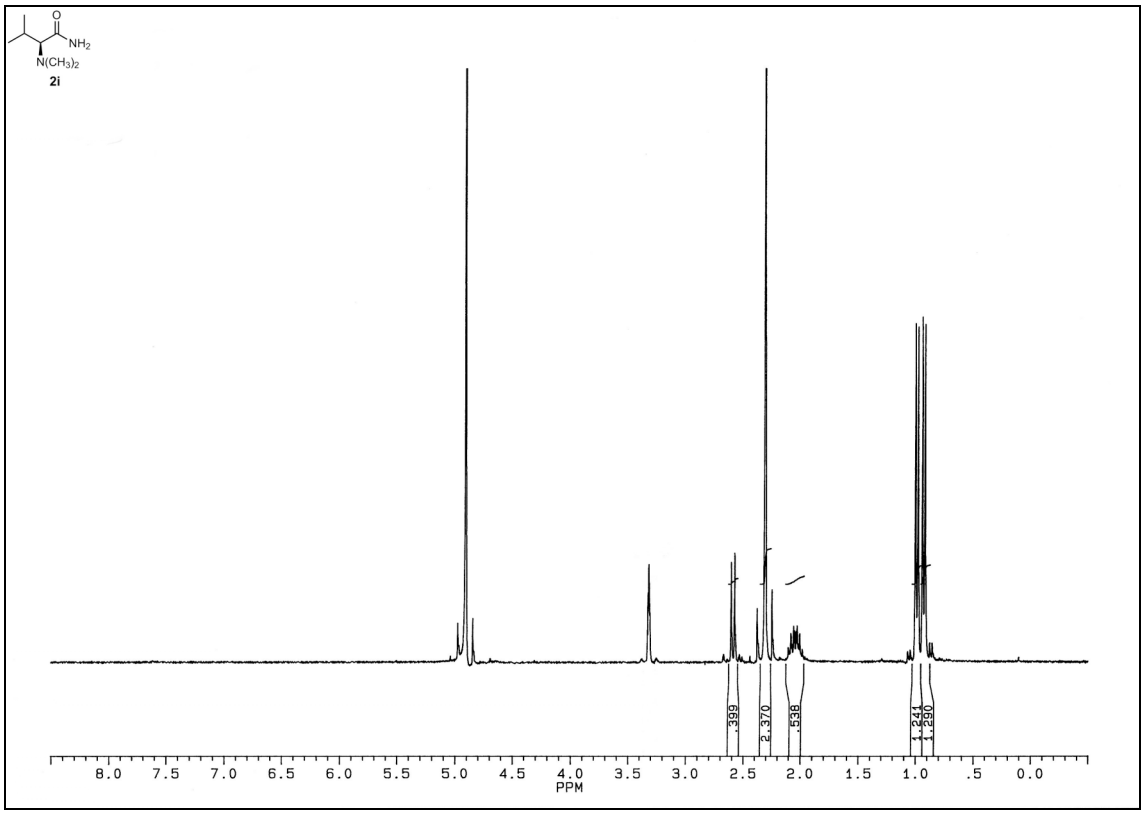
PPM


O
NH2
N(CH3)2
2i
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2.370
.538
1.241
1.290
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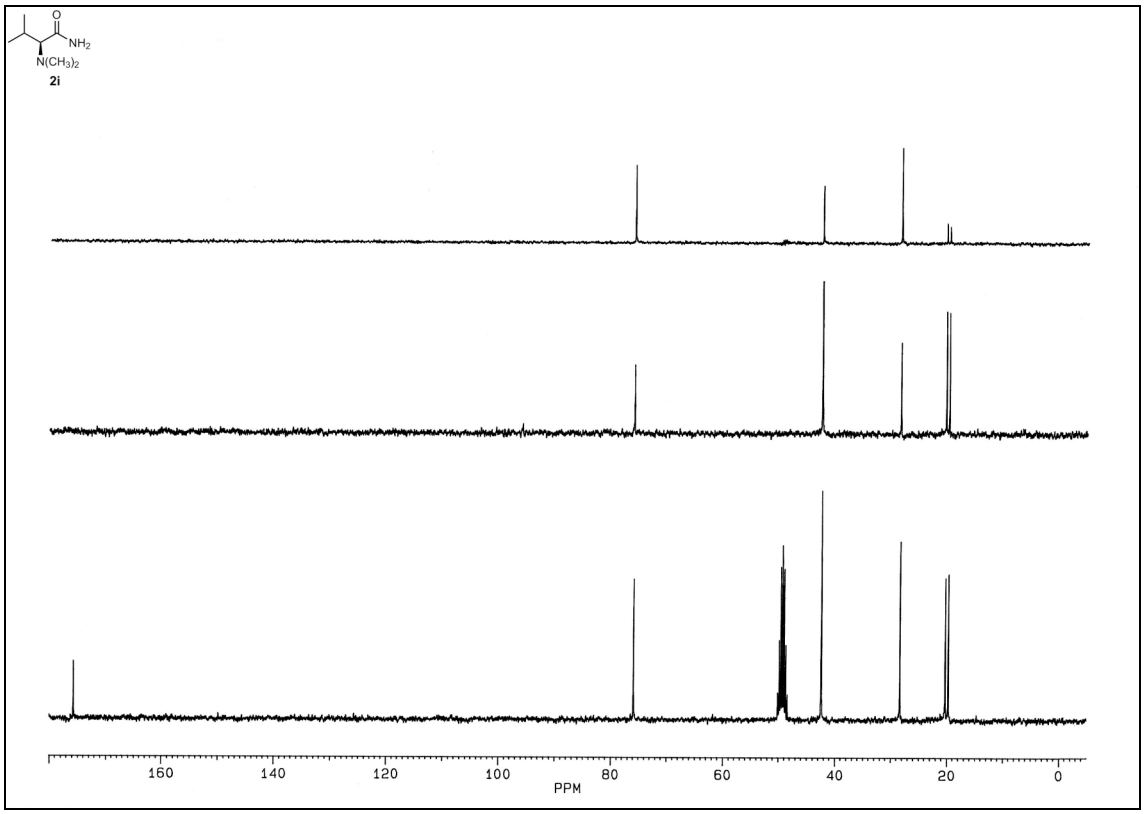
PPM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NH2
N(CH3)2
2i
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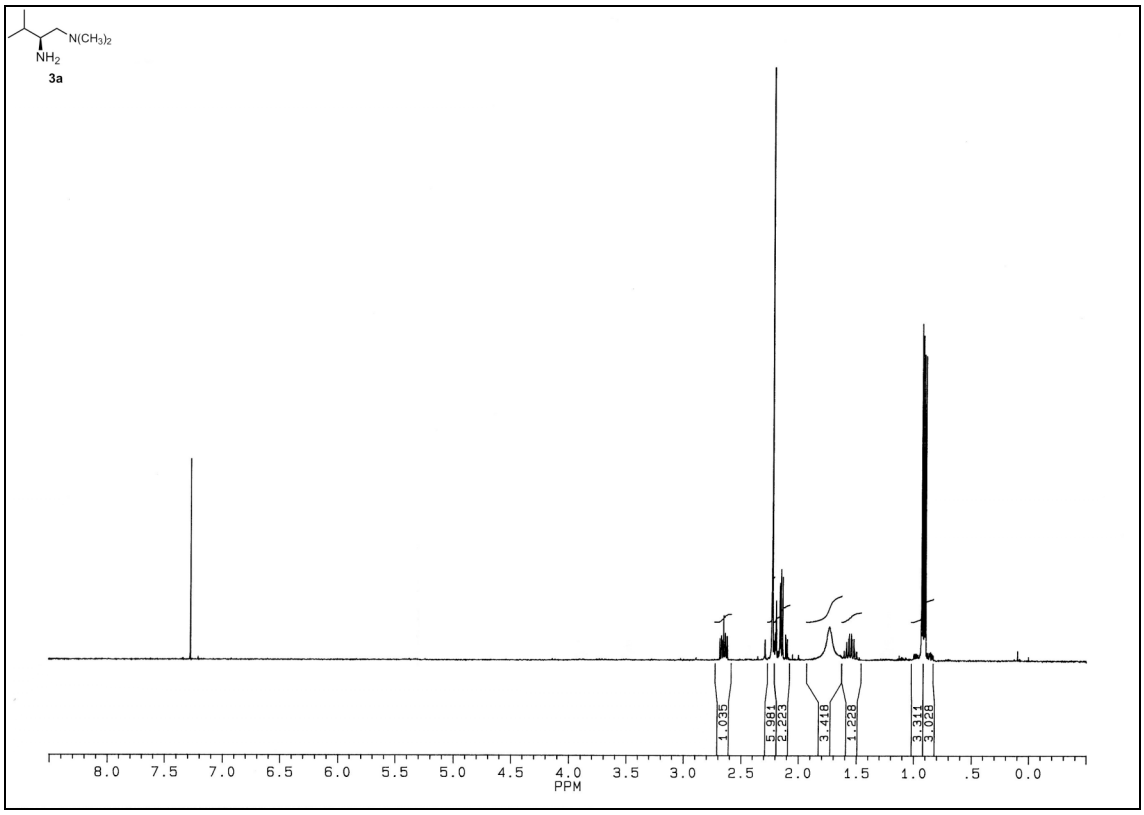
PPM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1.228
3.311
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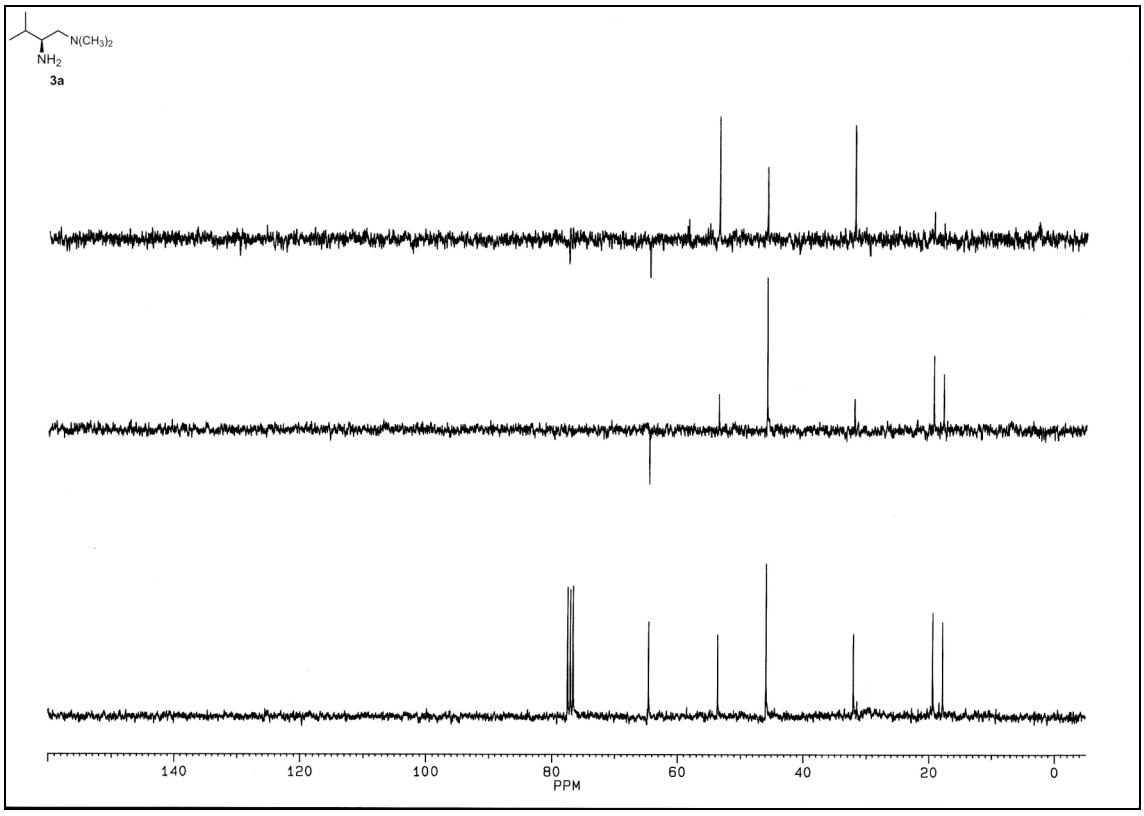
PPM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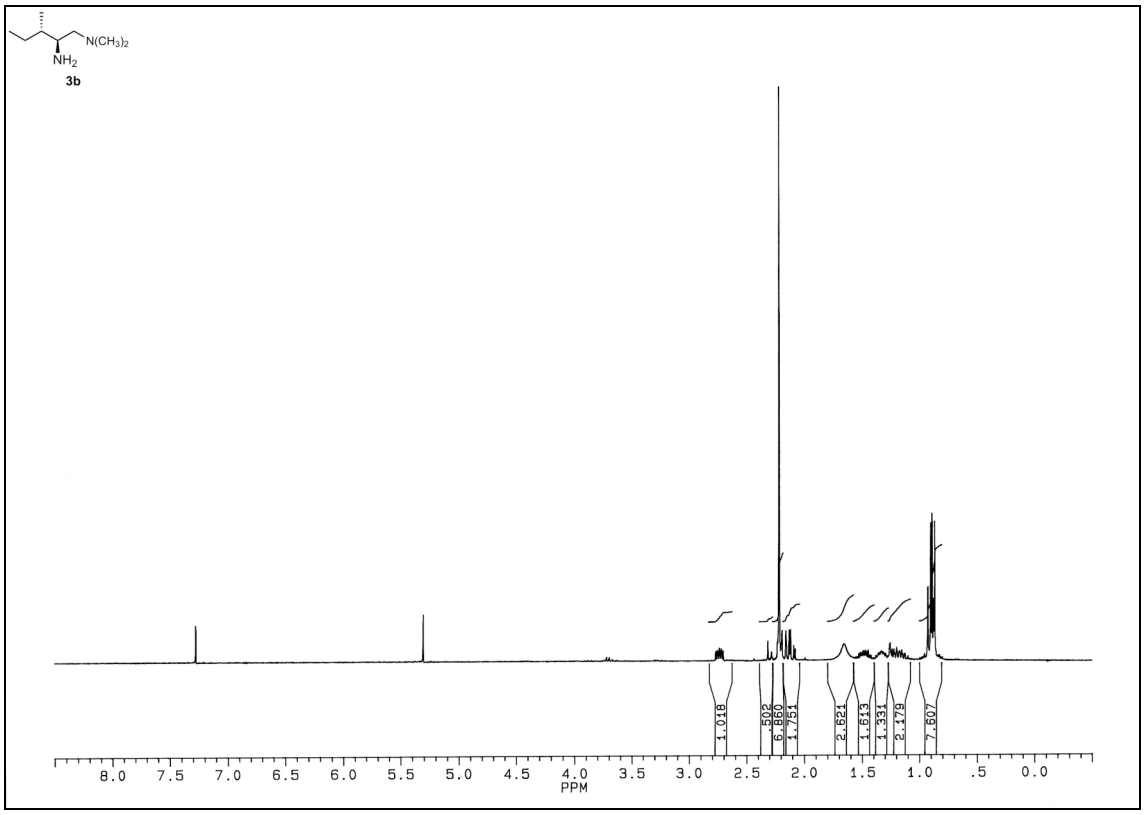
NH2
3a
140 120 100 80 60 40 20 0
PPM


N(CH3)2
NH2
3b
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6.860
1.751
2.621
1.613
1.331
2.479
7.607
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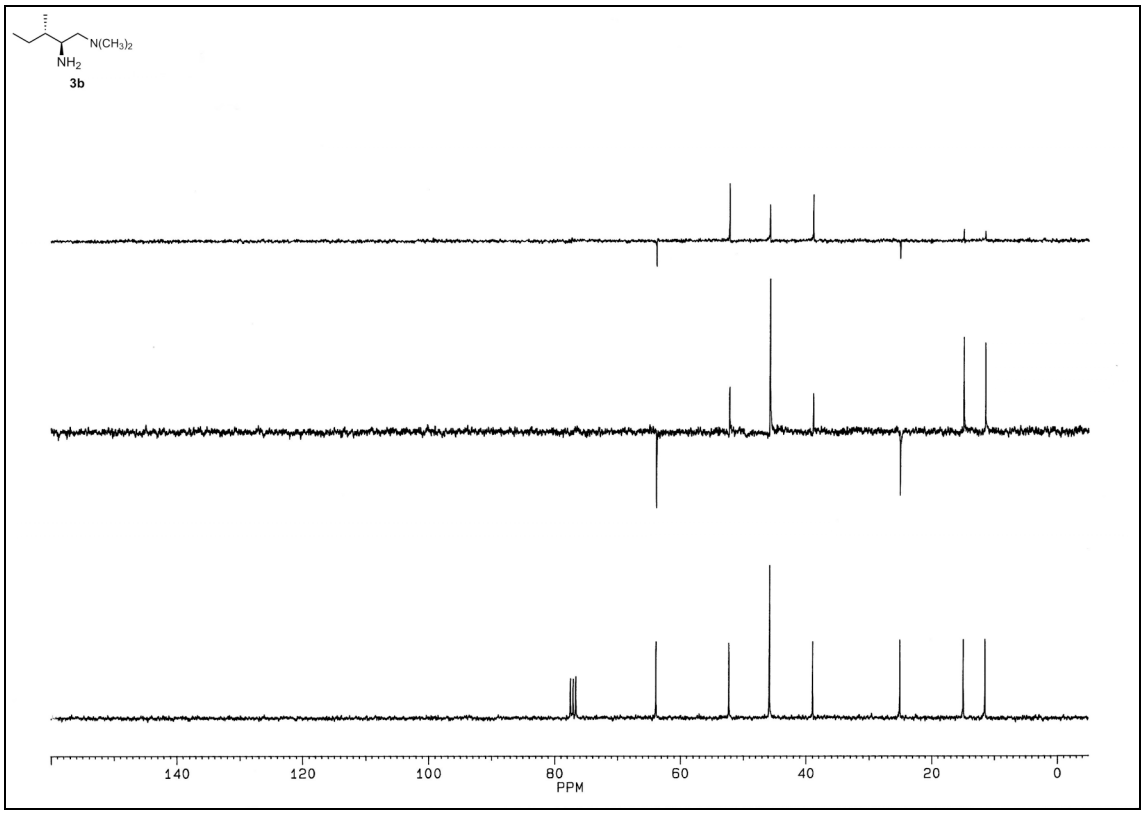
PPM


N(CH3)2
NH2
3b
140 120 100 80 60 40 20 0
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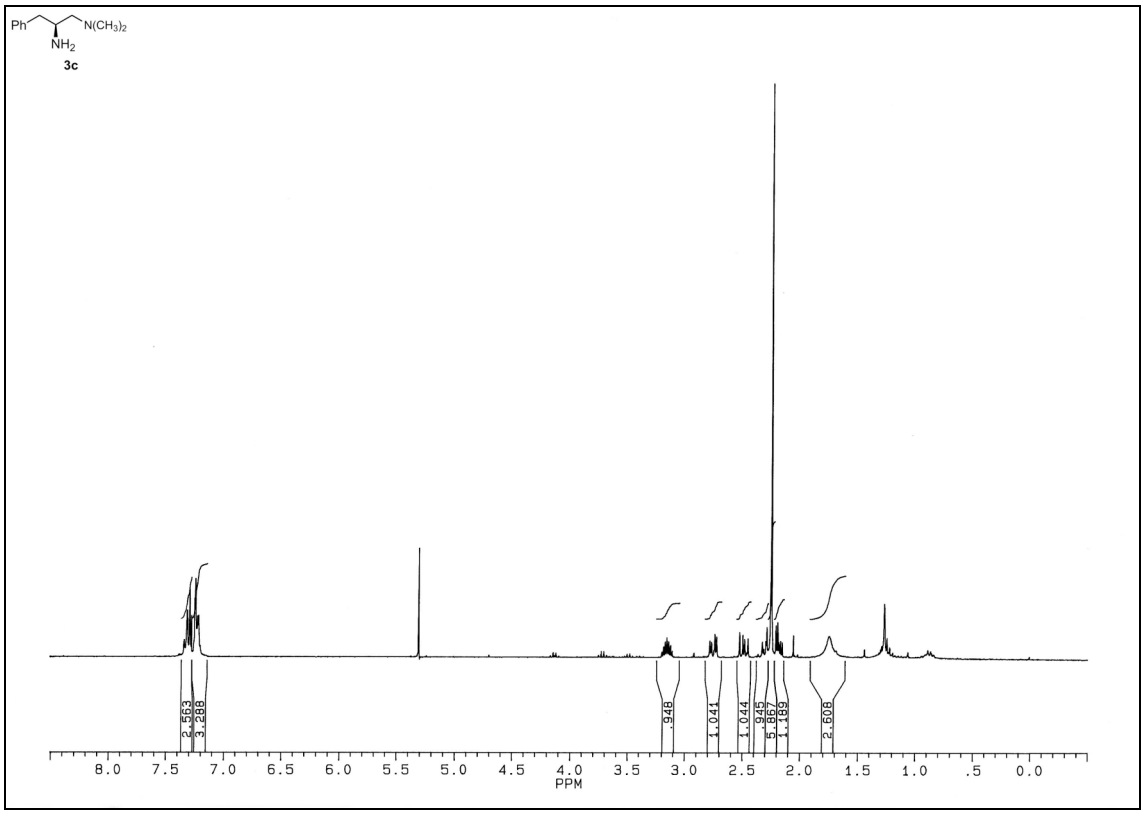
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NH2
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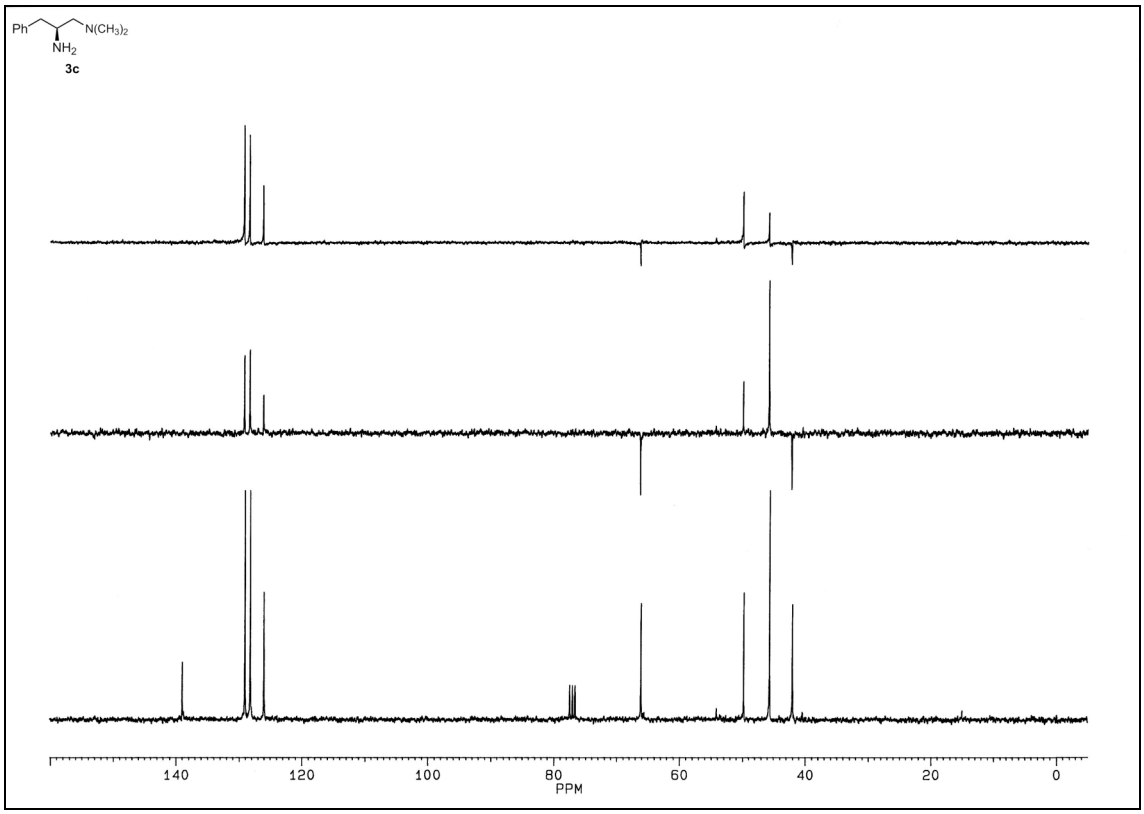
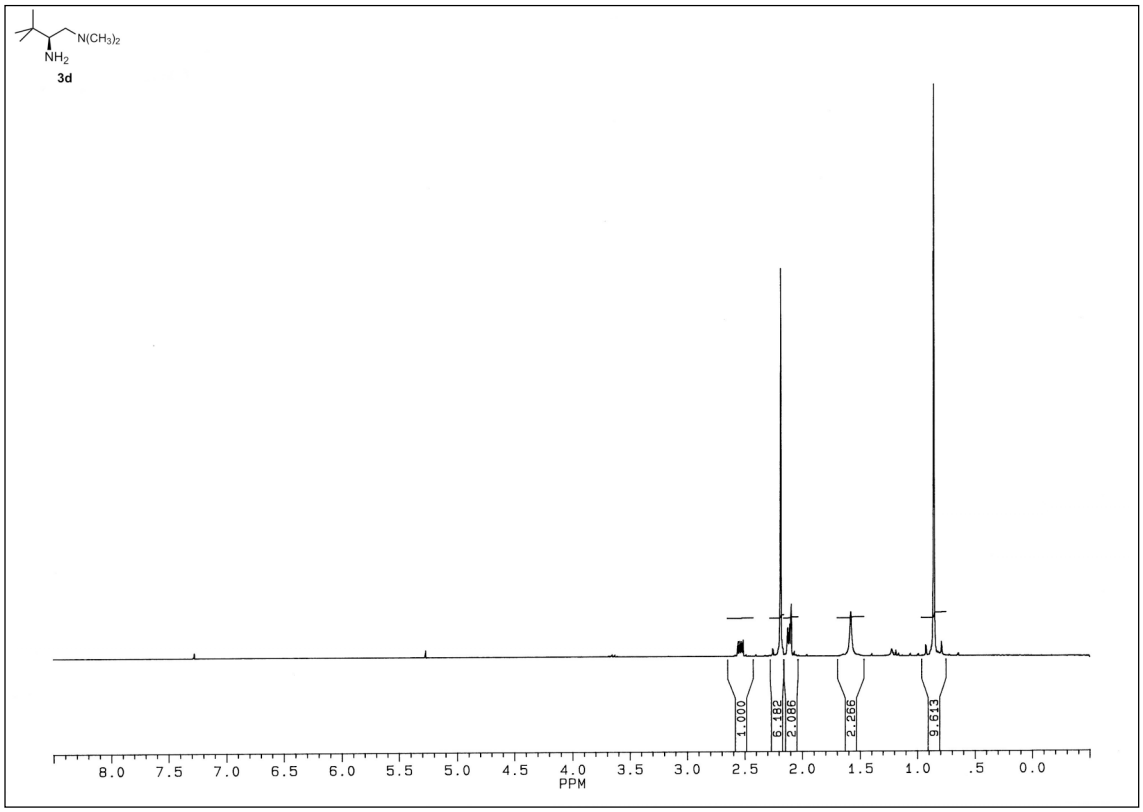
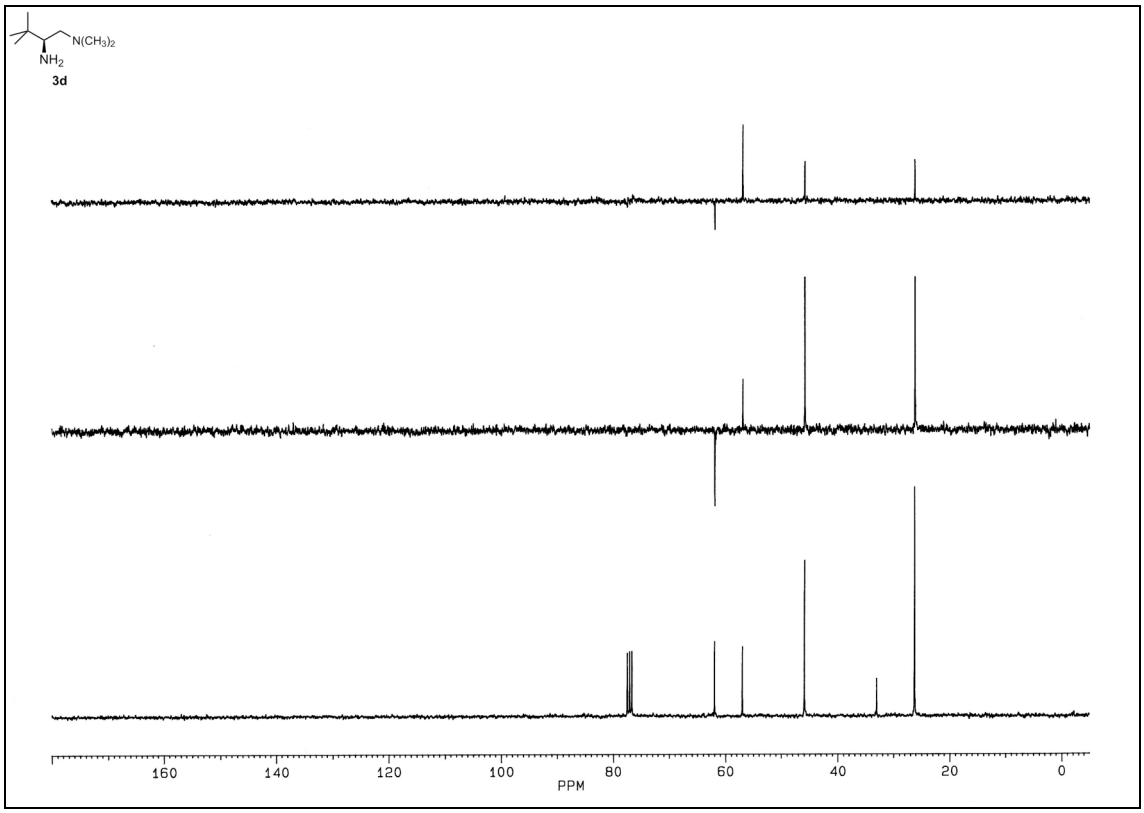
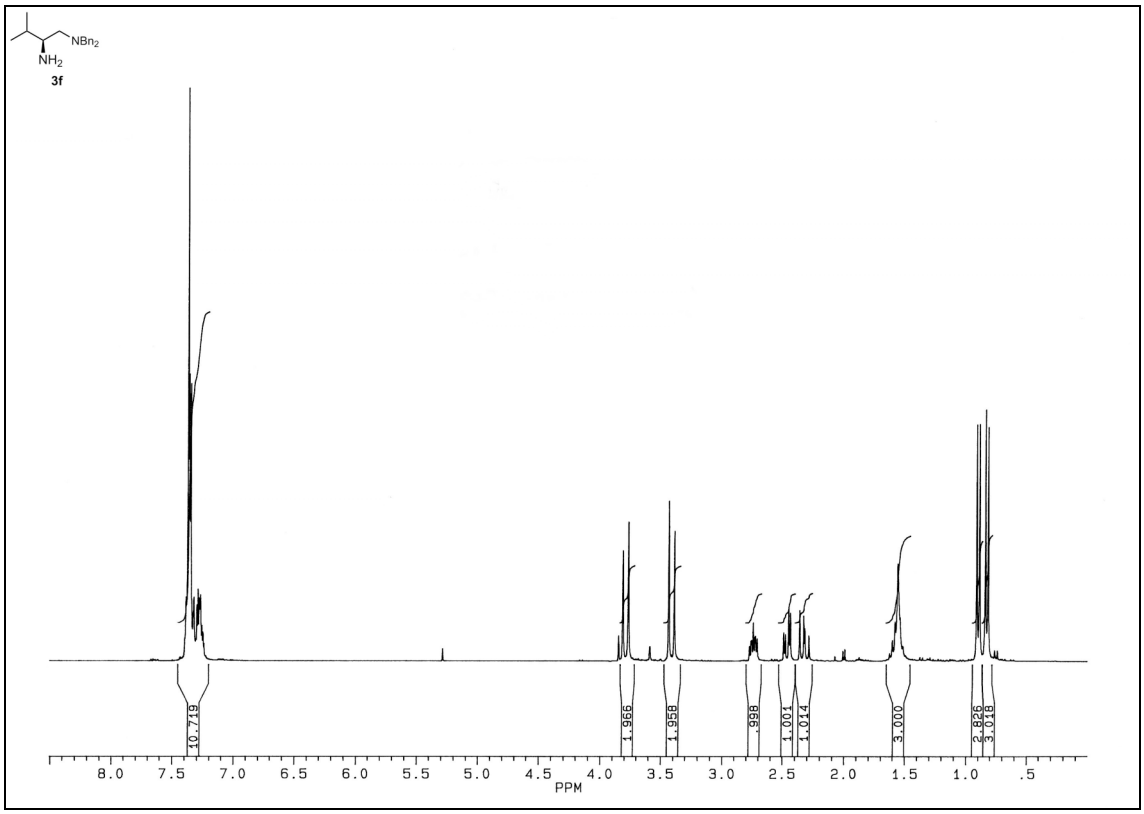
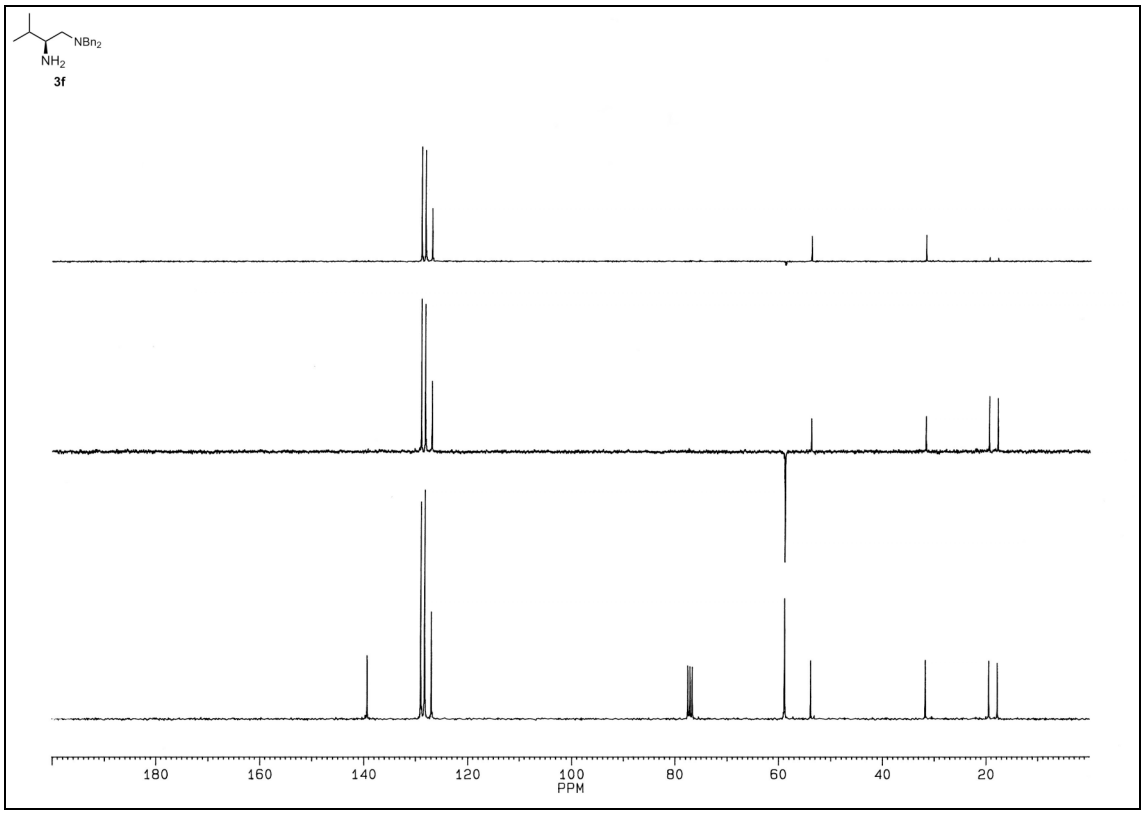
1.041
1.044
.945
5.687
1.189
2.608
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5 0.0
PPM

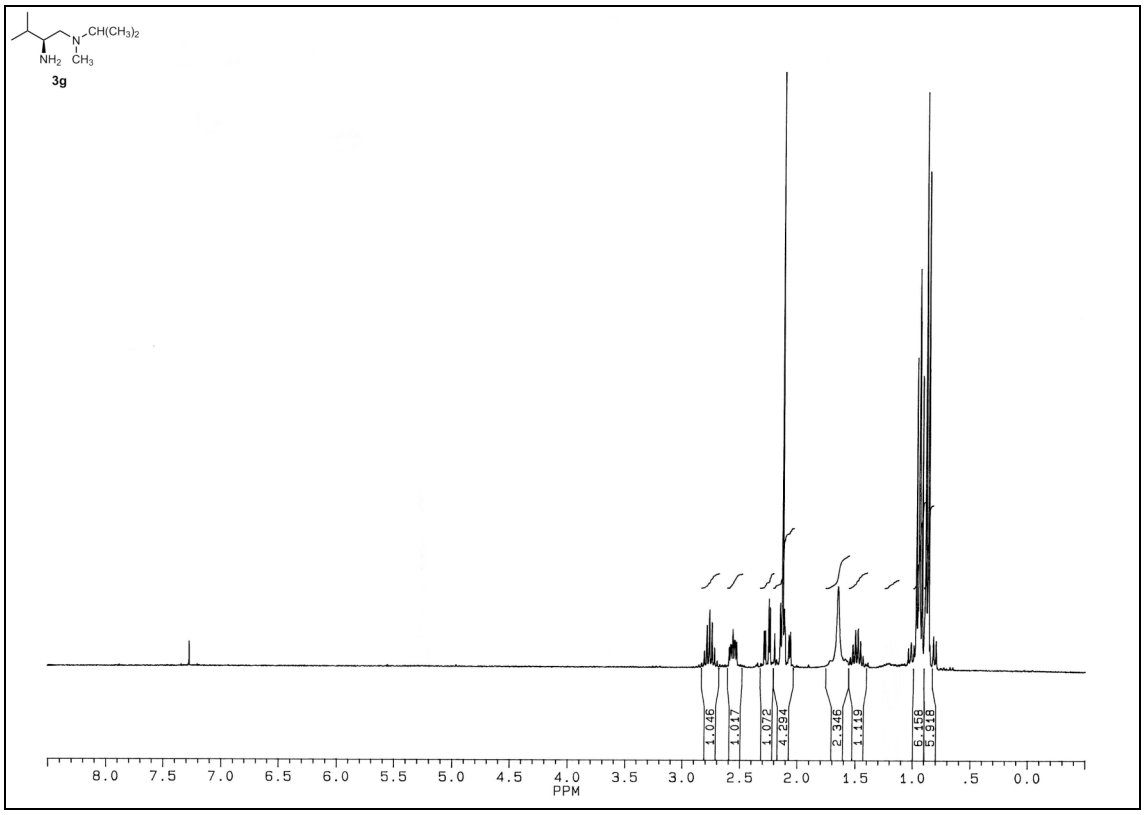

Ph
N(CH3)2
NH2
3c
140 120 100 80 60 40 20 0
PPM

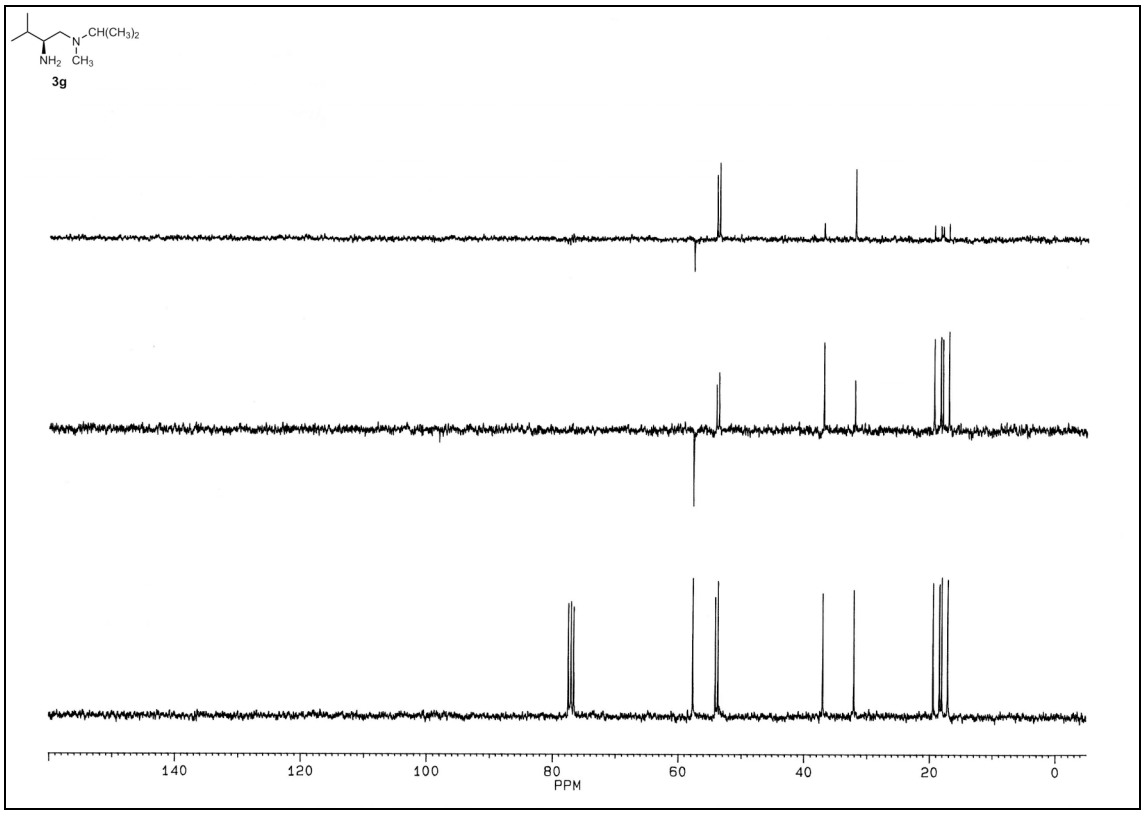

N(CH3)2
NH2
3d
1.000
6.182
2.086
2.266
9.613
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5 0.0
PPM

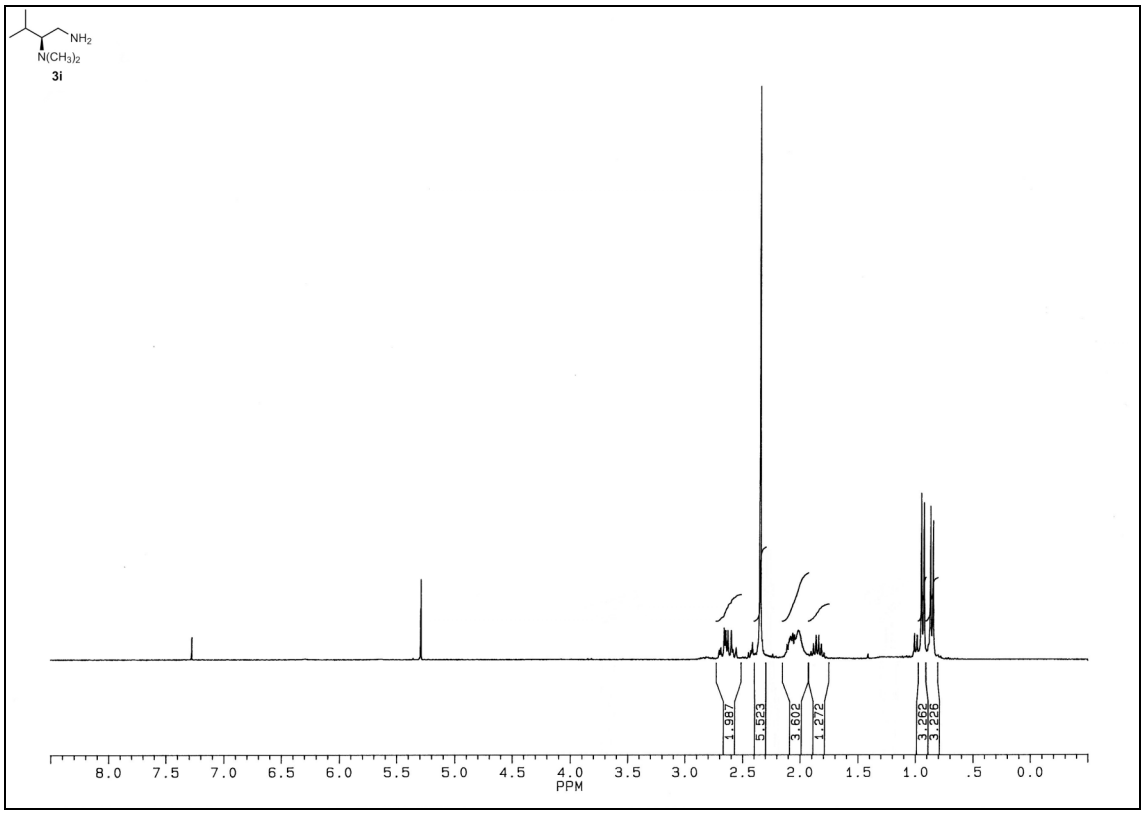

N(CH3)2
NH2
3d
160 140 120 100 80 60 40 20 0
PPM

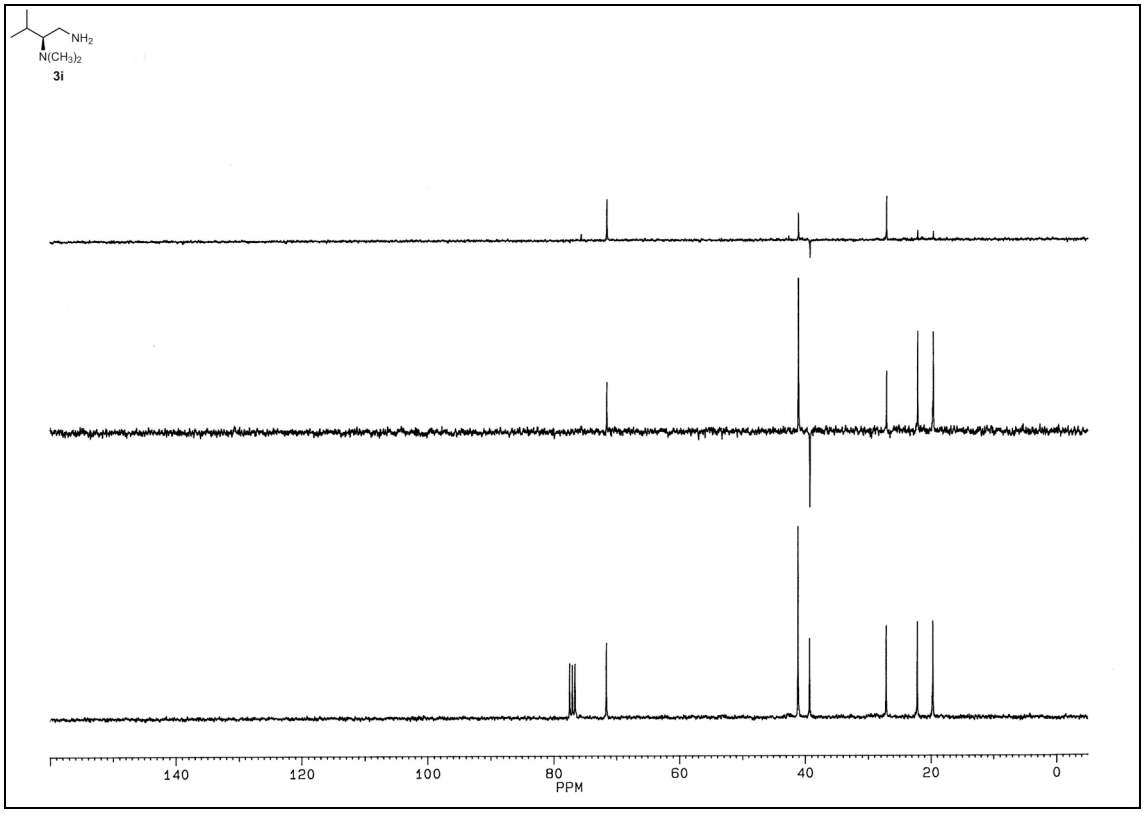

NBn2
NH2
3f
10.719
1.966
1.958
.998
1.001
1.014
3.000
2.826
3.018
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
PPM


NBn2
NH2
3f
180
160
140
120
100
80
60
40
20
PPM

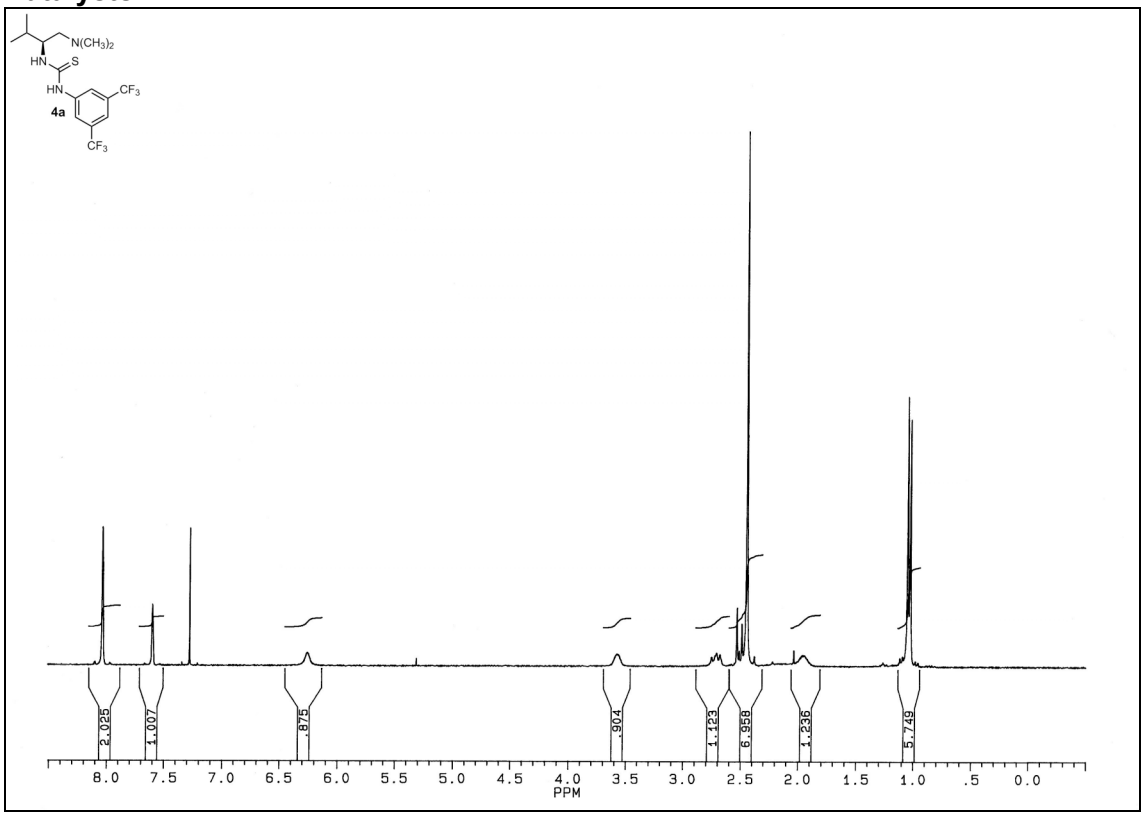

3g
1.046
1.017
1.072
4.294
2.346
1.119
6.158
5.918
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5 0.0
PPM

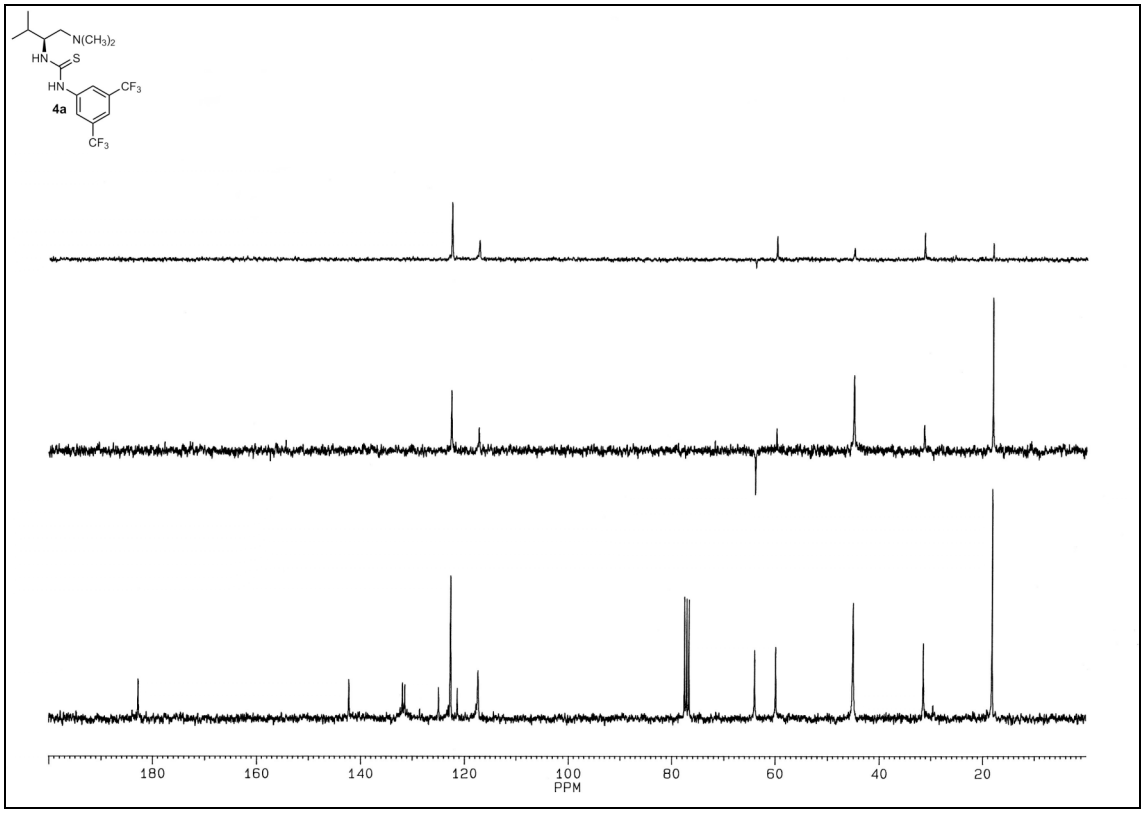

3g
140 120 100 80 60 40 20 0
PPM

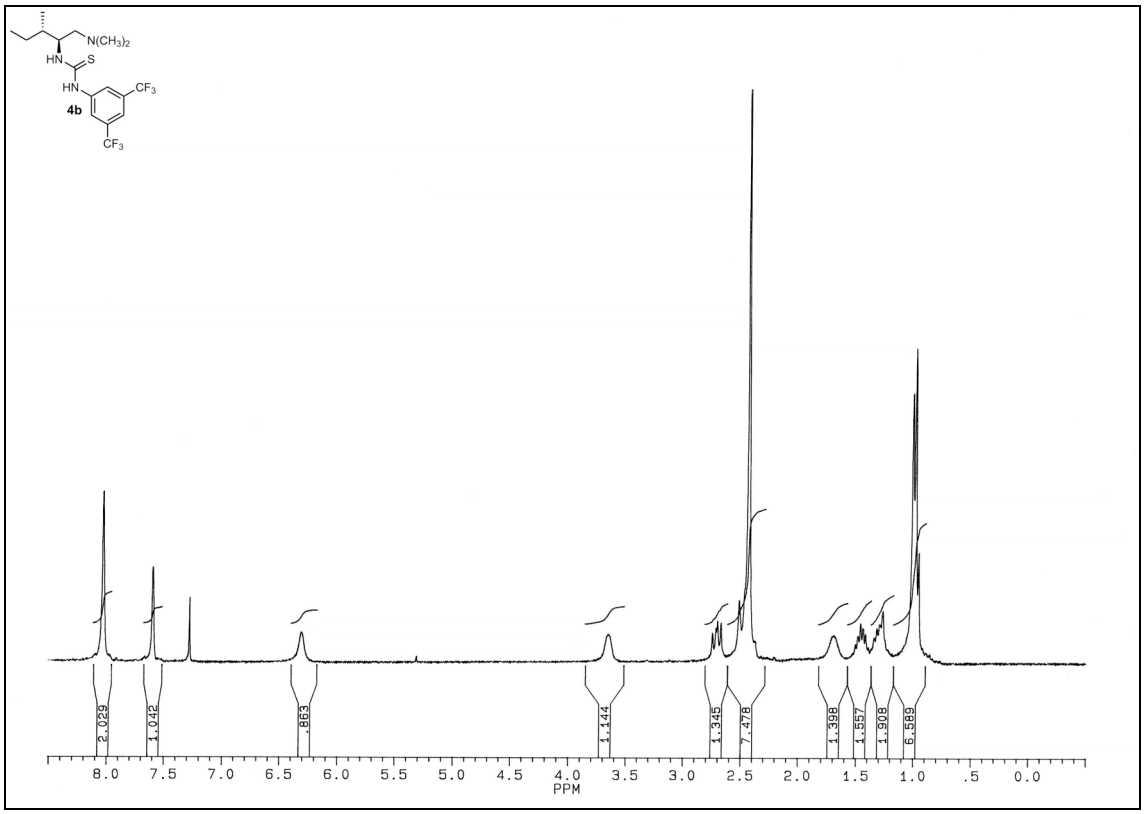

NH2
N(CH3)2
3i
1.987
5.523
3.602
1.272
3.262
3.226
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5 0.0
PPM

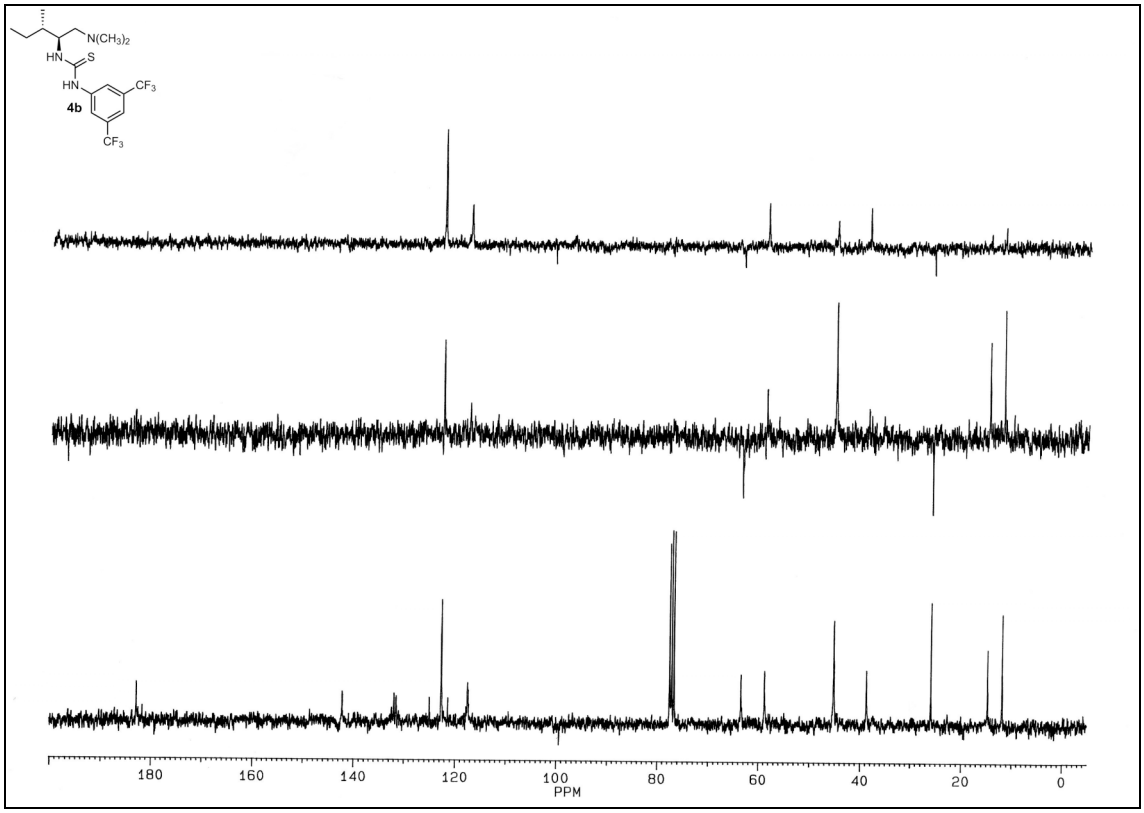

NH2
N(CH3)2
3i
140 120 100 80 60 40 20 0
PPM

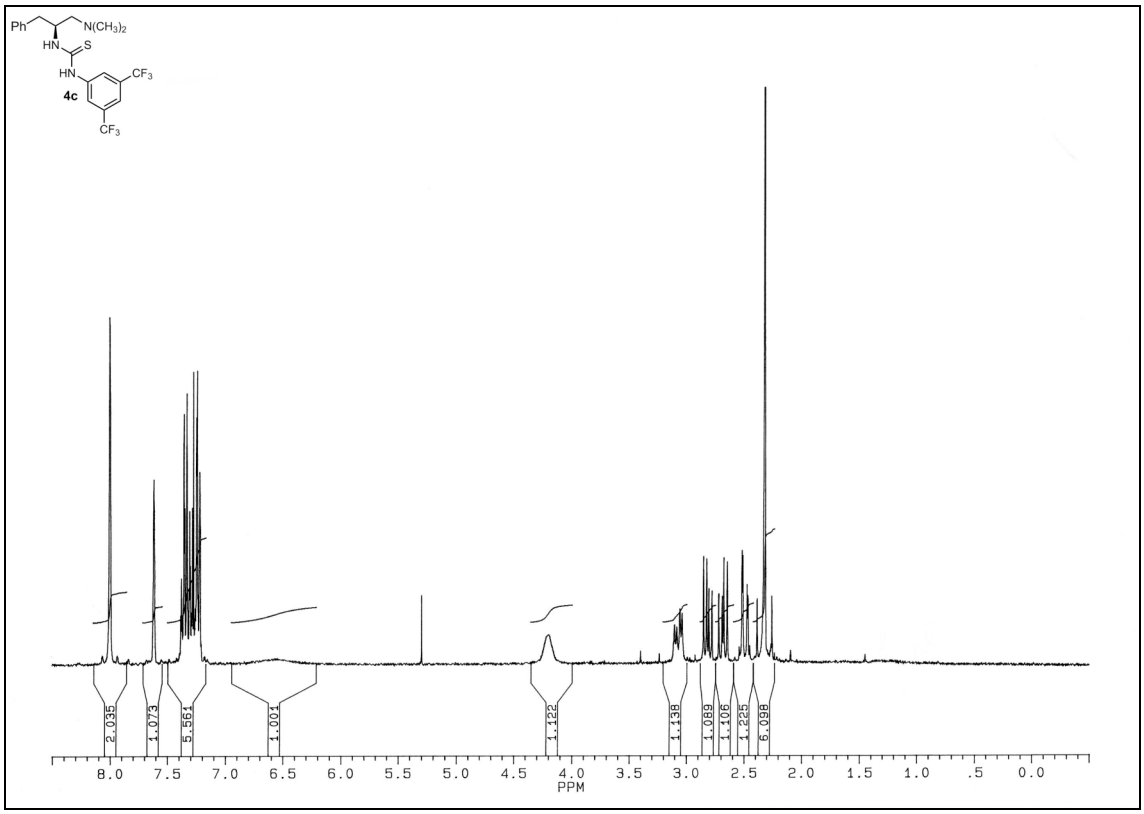
Catalysts 4

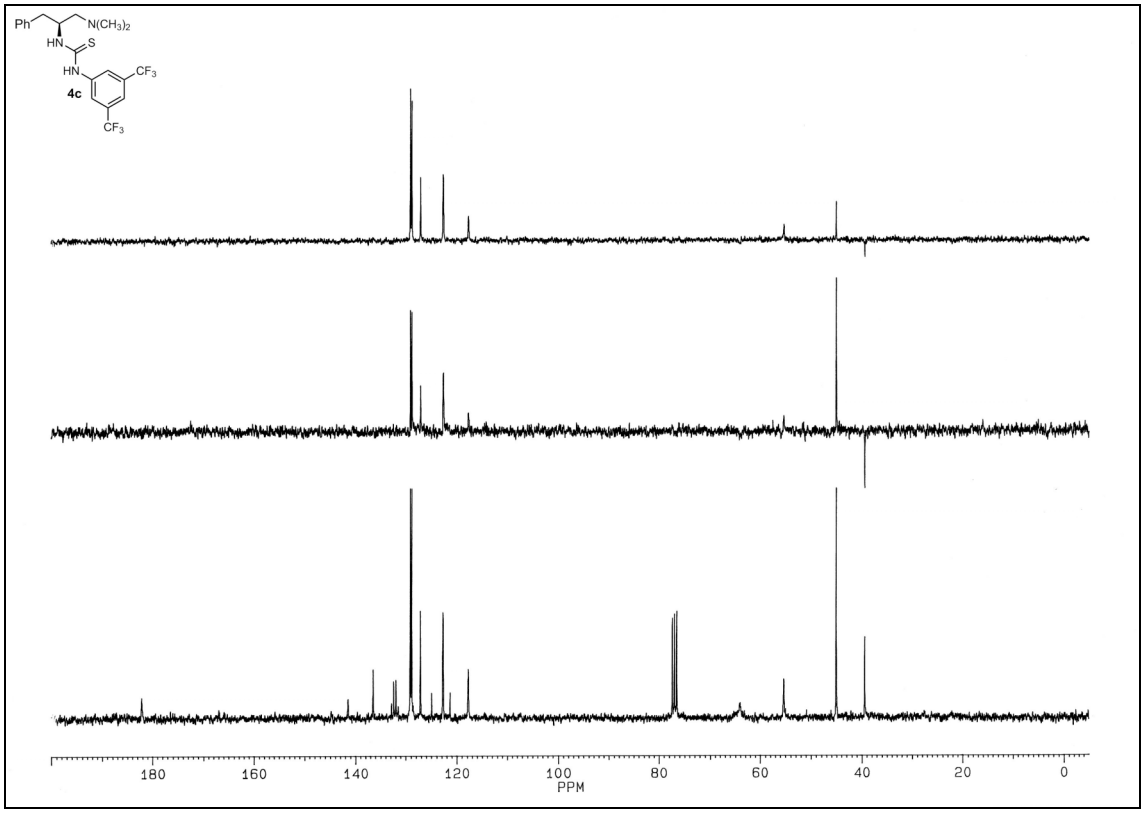

N(CH3)2
HN
S
HN
CF3
4a
CF3
2.025
1.007
.875
.904
1.123
6.958
1.236
5.749
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
PPM

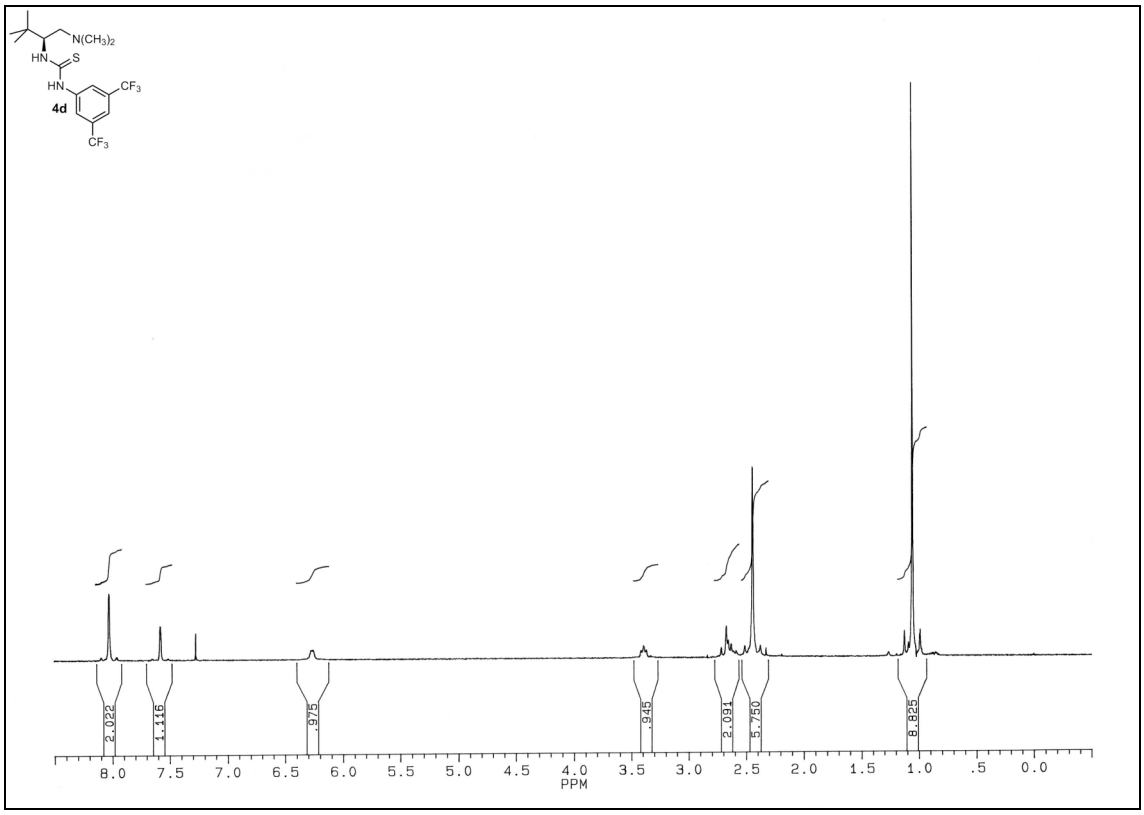

N(CH3)2
HN
S
HN
CF3
4a
CF3
180
160
140
120
100
80
60
40
20
PPM

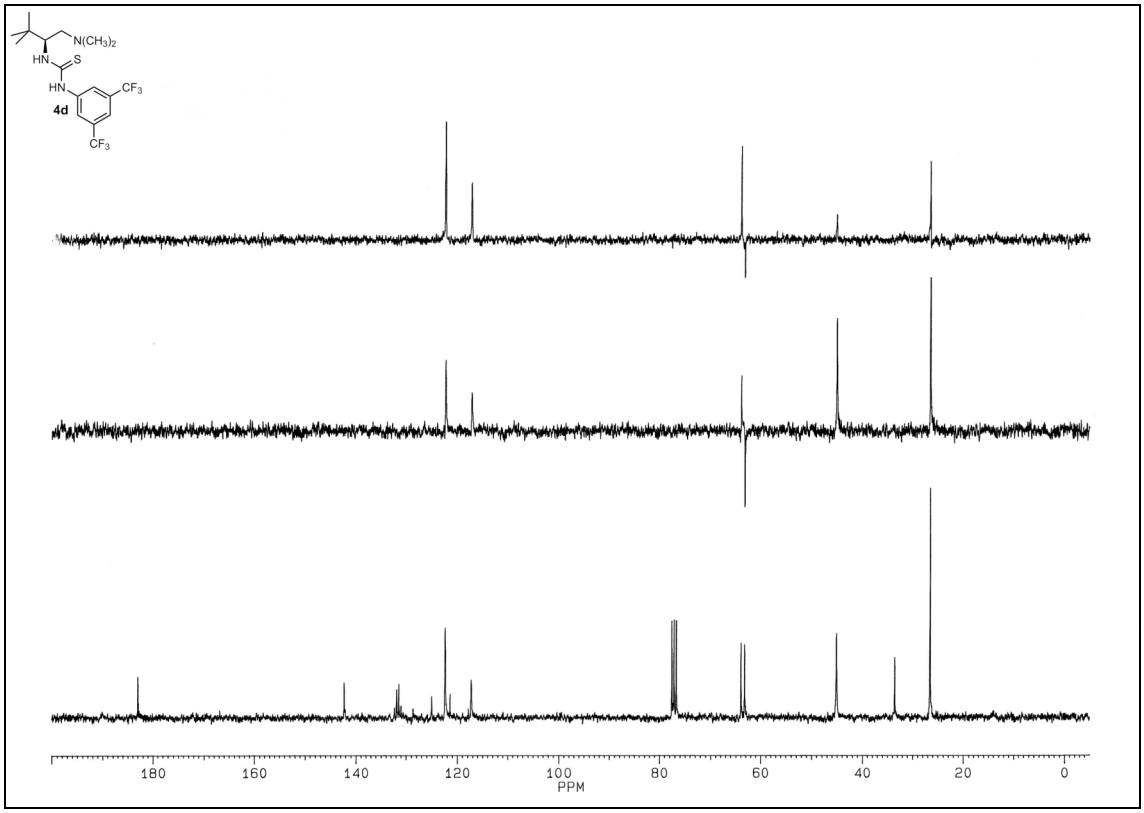

N(CH3)2
HN
S
HN
CF3
CF3
4b
2.029
1.042
.863
1.444
1.345
7.478
1.398
1.557
1.908
6.589
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5 0.0
PPM

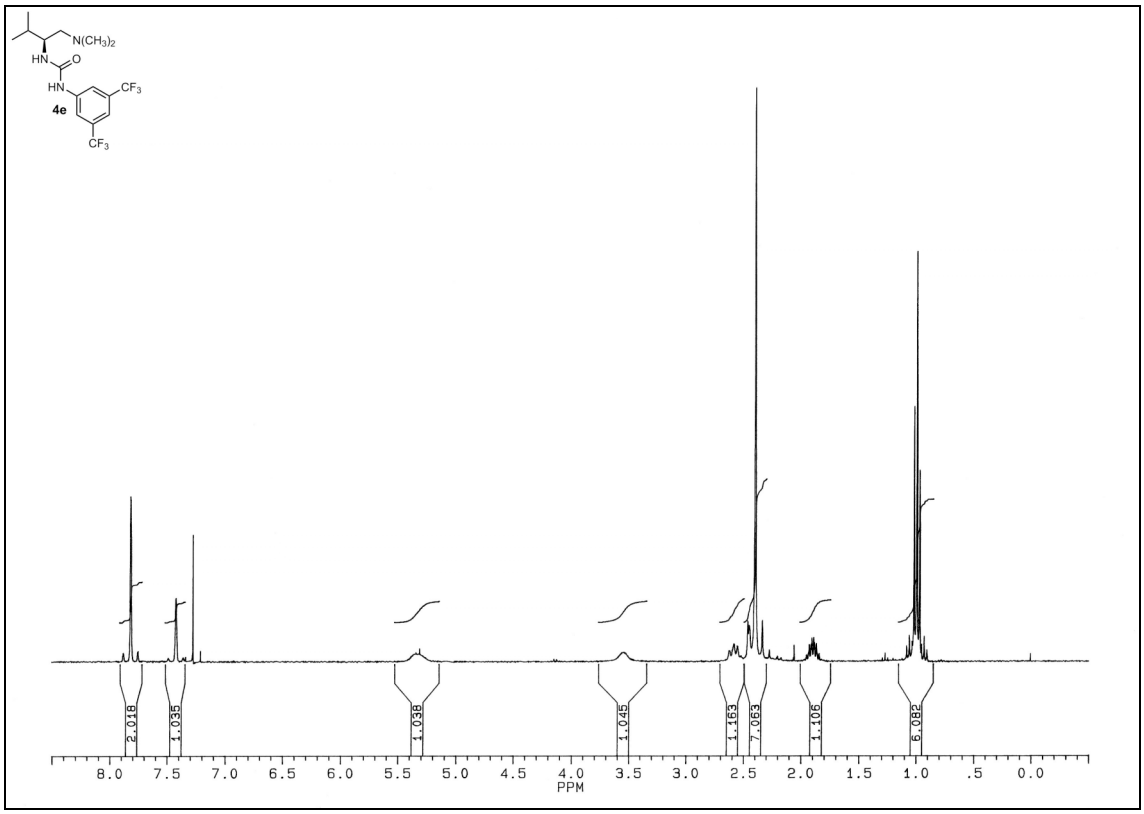

N(CH3)2
HN
S
HN
CF3
CF3
4b
180 160 140 120 100 80 60 40 20 0
PPM

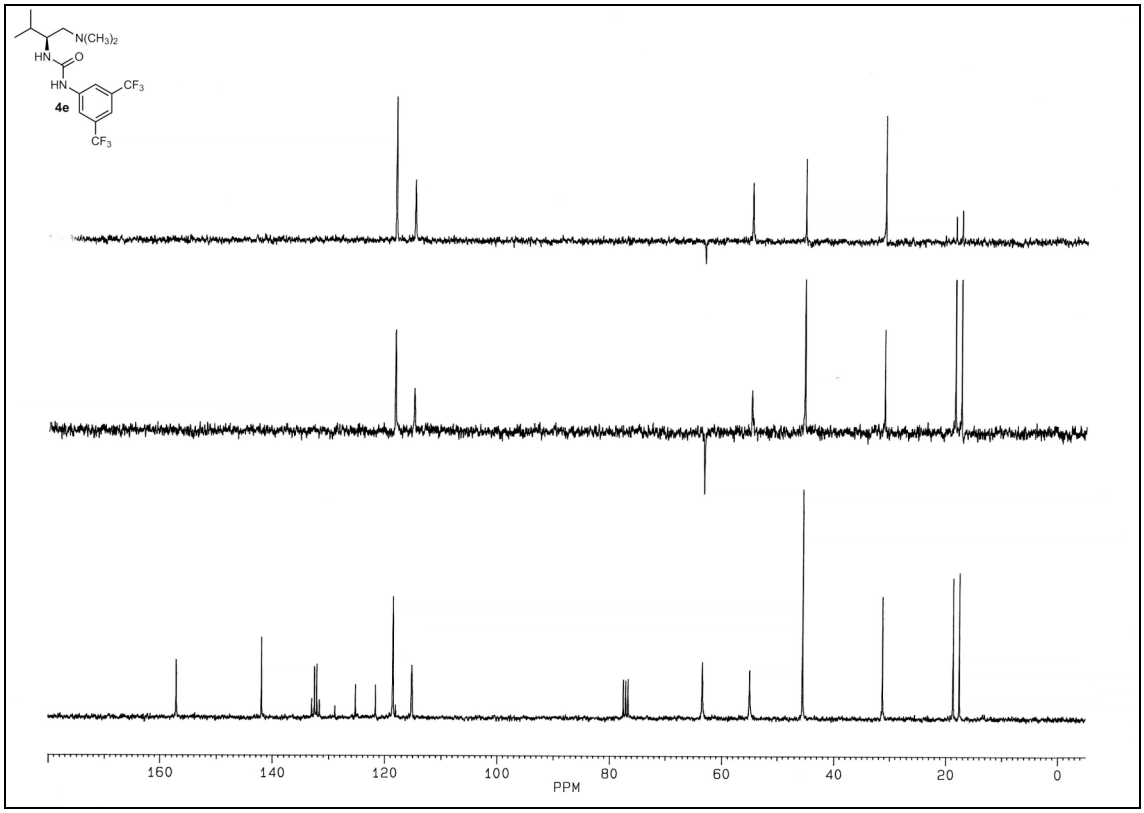

Ph
N(CH3)2
HN
S
HN
CF3
CF3
4c
2.035
1.073
5.561
4.001
1.122
1.138
1.089
1.106
1.225
6.098
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
PPM

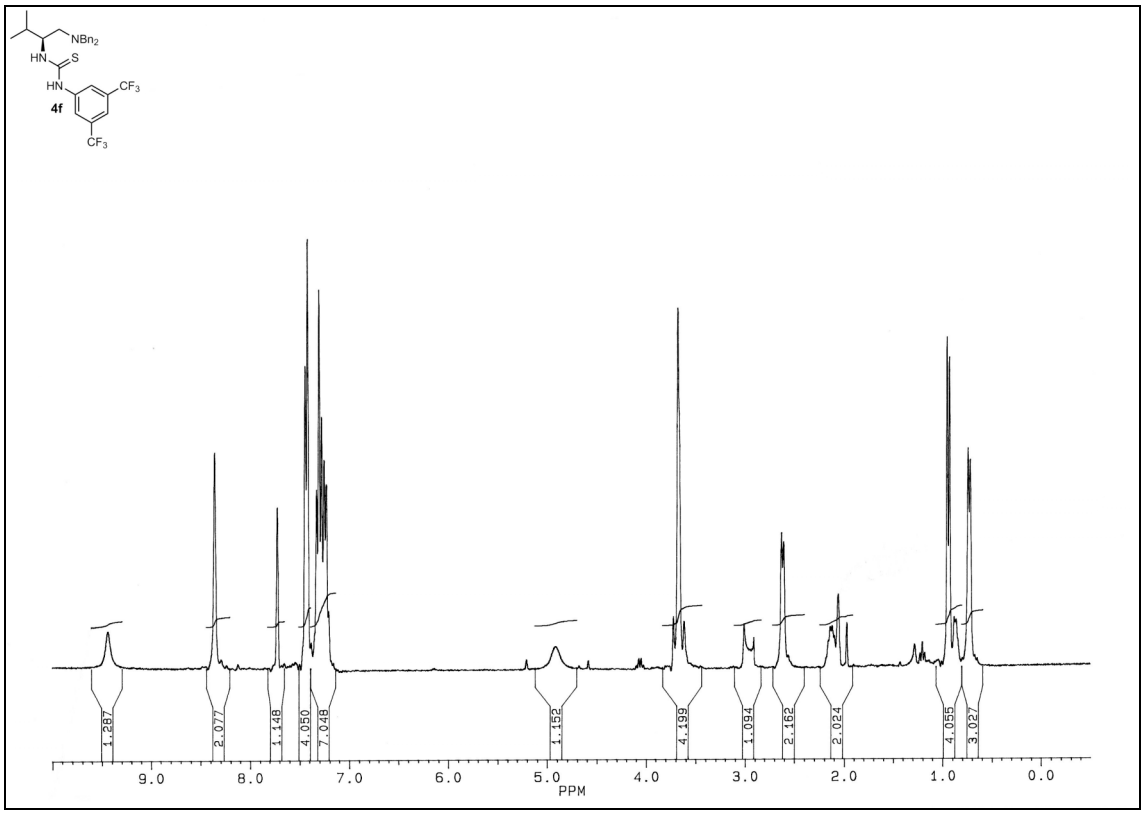

Ph
N(CH3)2
HN
S
HN
CF3
CF3
4c
180
160
140
120
100
80
60
40
20
0
PPM

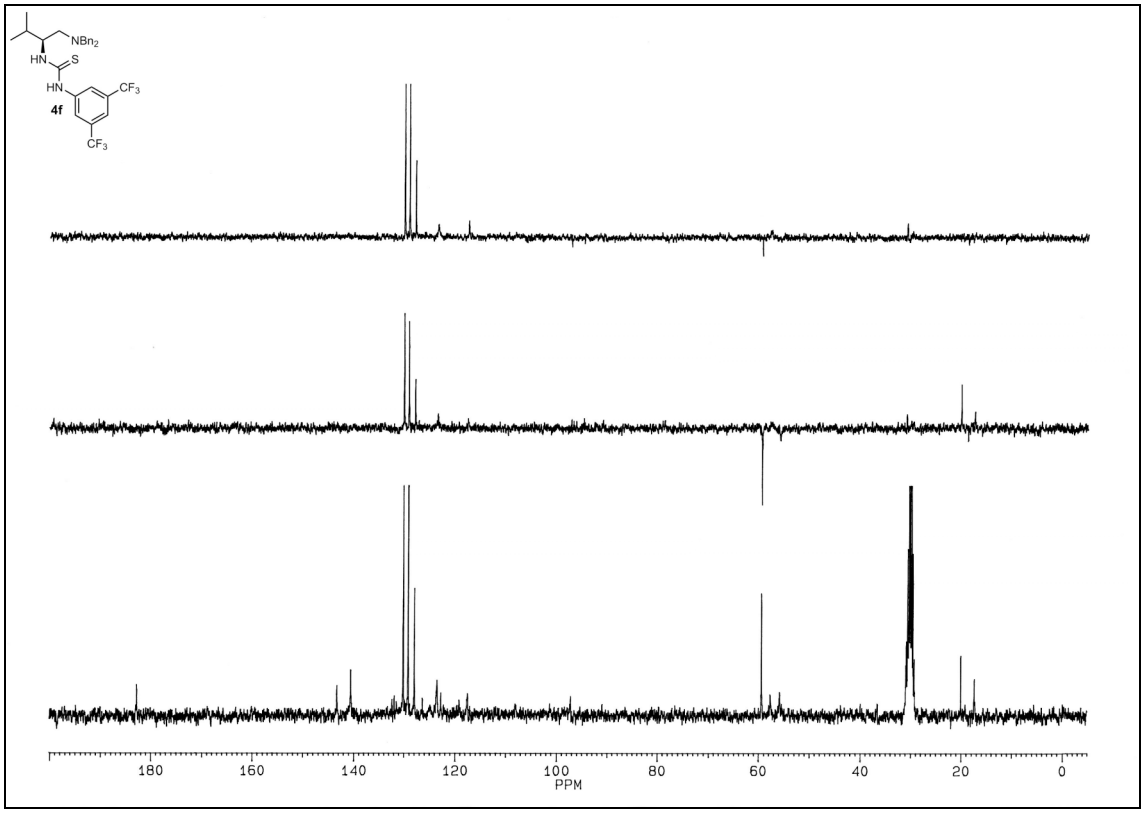

4d
2.022
1.116
.975
.945
2.091
5.750
8.825
PPM

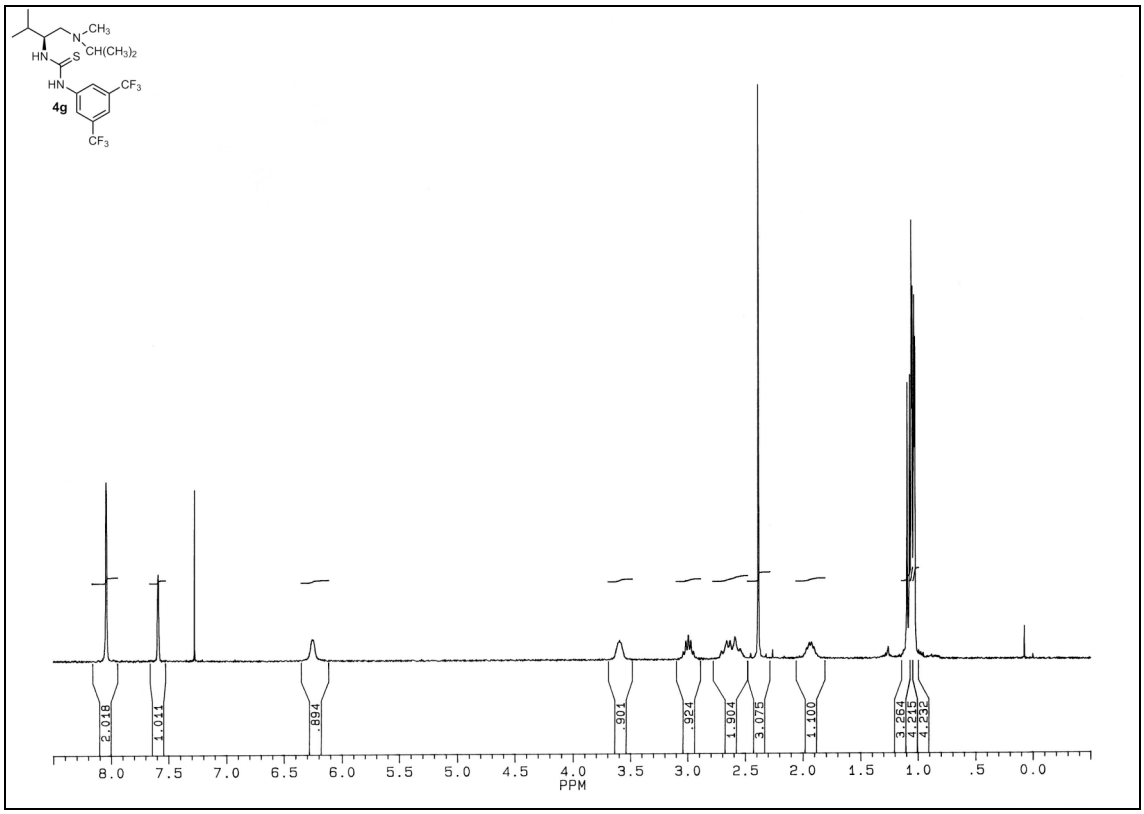

4d
PPM

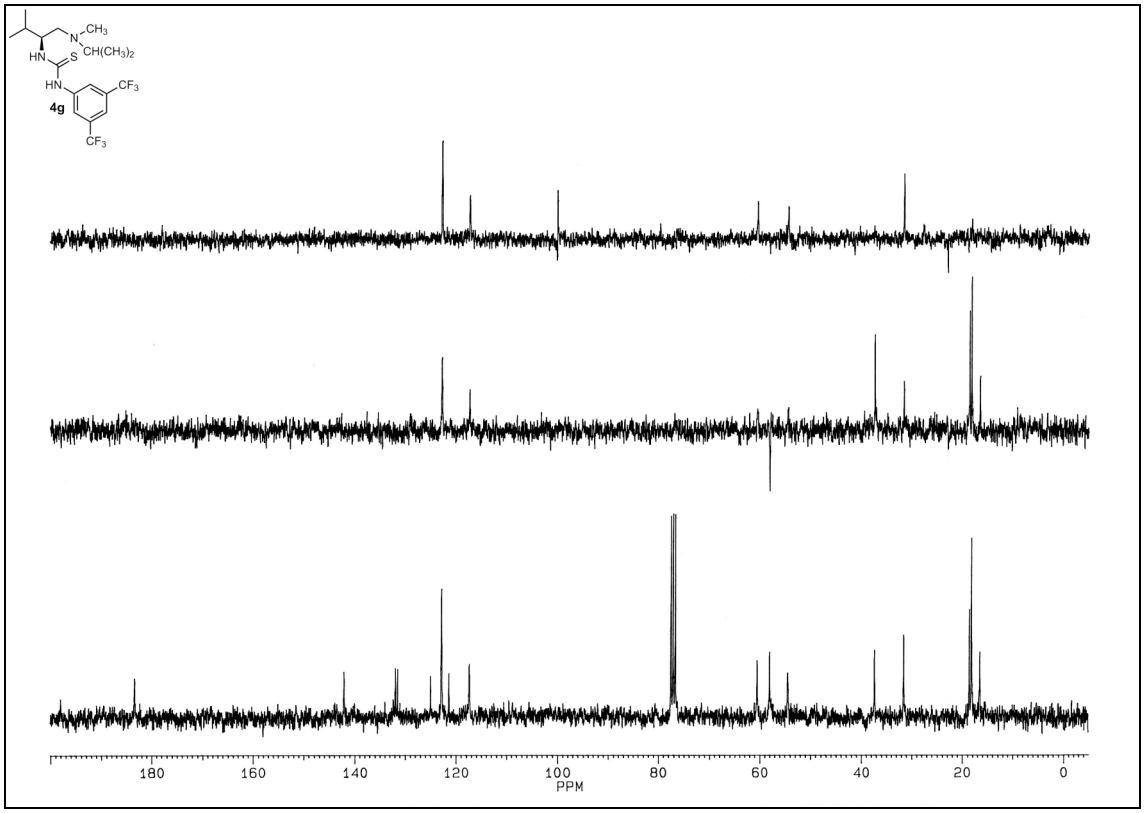

N(CH3)2
HN
O
HN
CF3
CF3
4e
2.018
1.035
1.038
1.045
1.163
7.063
1.106
6.082
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5 0.0
PPM

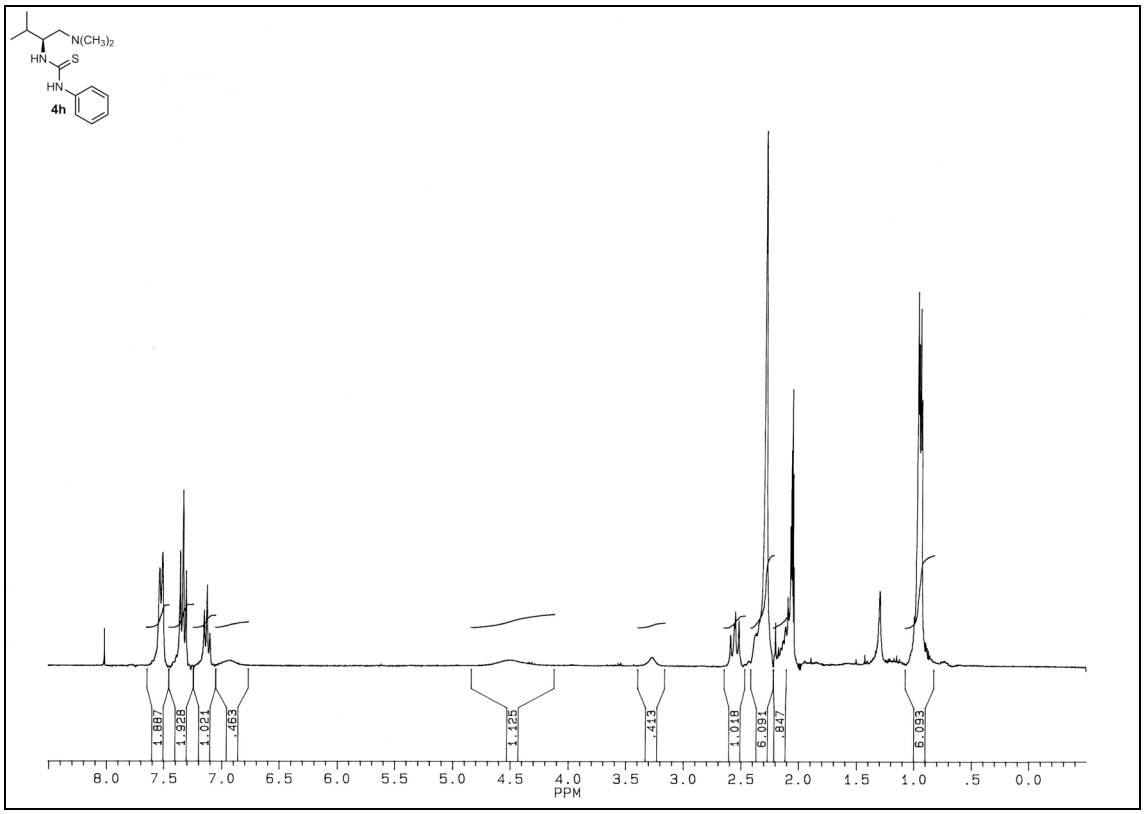

N(CH3)2
HN
O
HN
CF3
CF3
4e
160 140 120 100 80 60 40 20 0
PPM

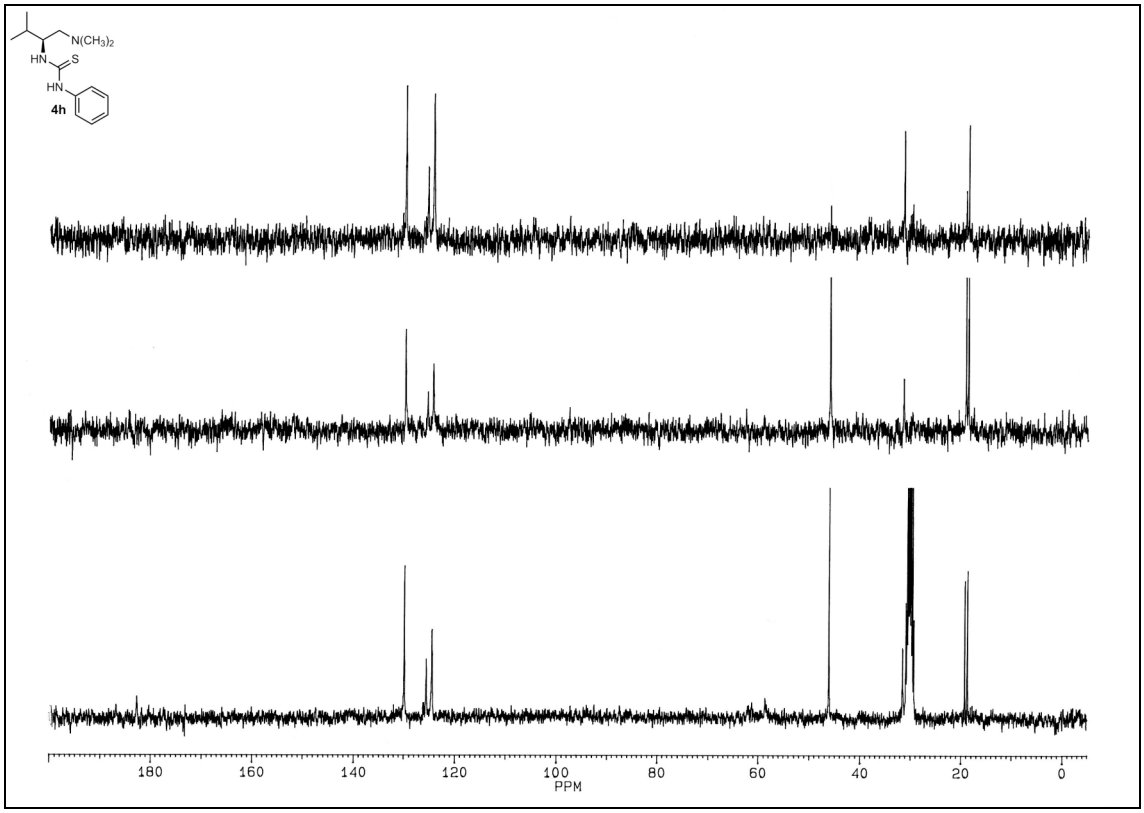

NBn2
HN
S
HN
CF3
CF3
4f
1.287
2.077
1.148
4.050
7.048
1.152
4.199
1.094
2.162
2.024
4.055
3.027
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

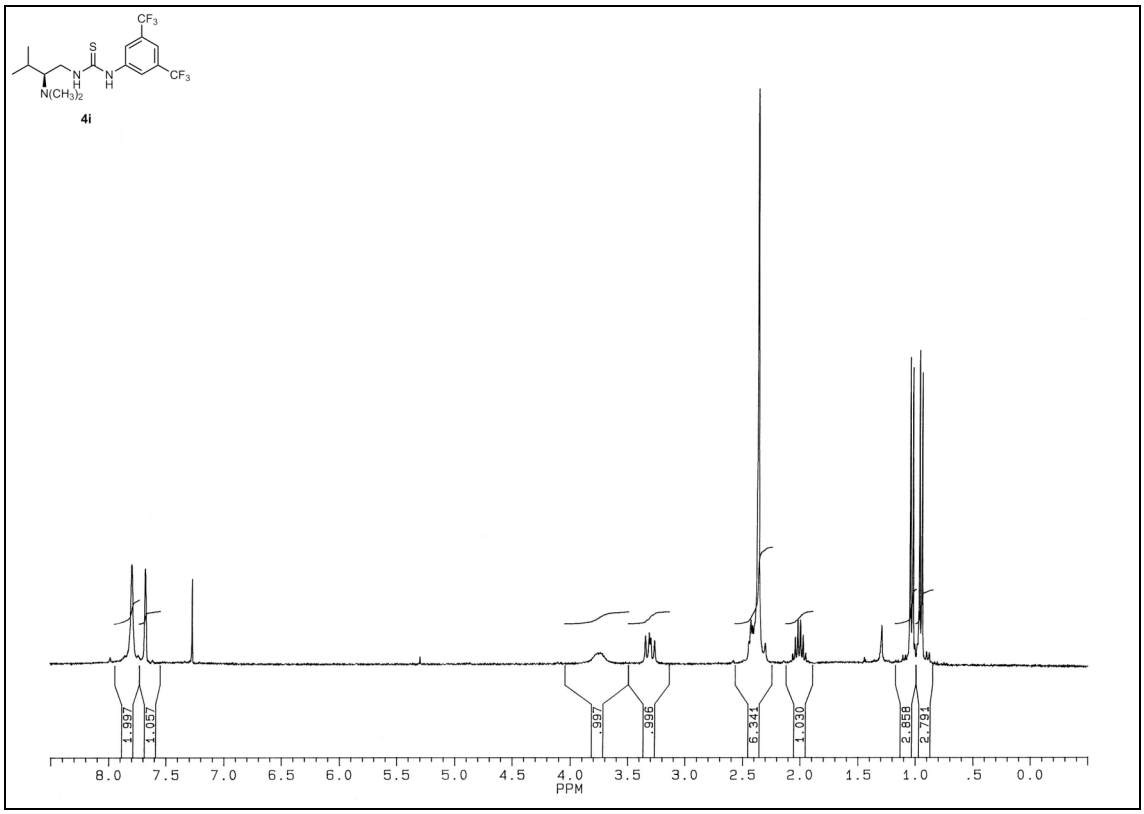

NBn2
HN
S
HN
CF3
CF3
4f
180
160
140
120
100
80
60
40
20
0
PPM

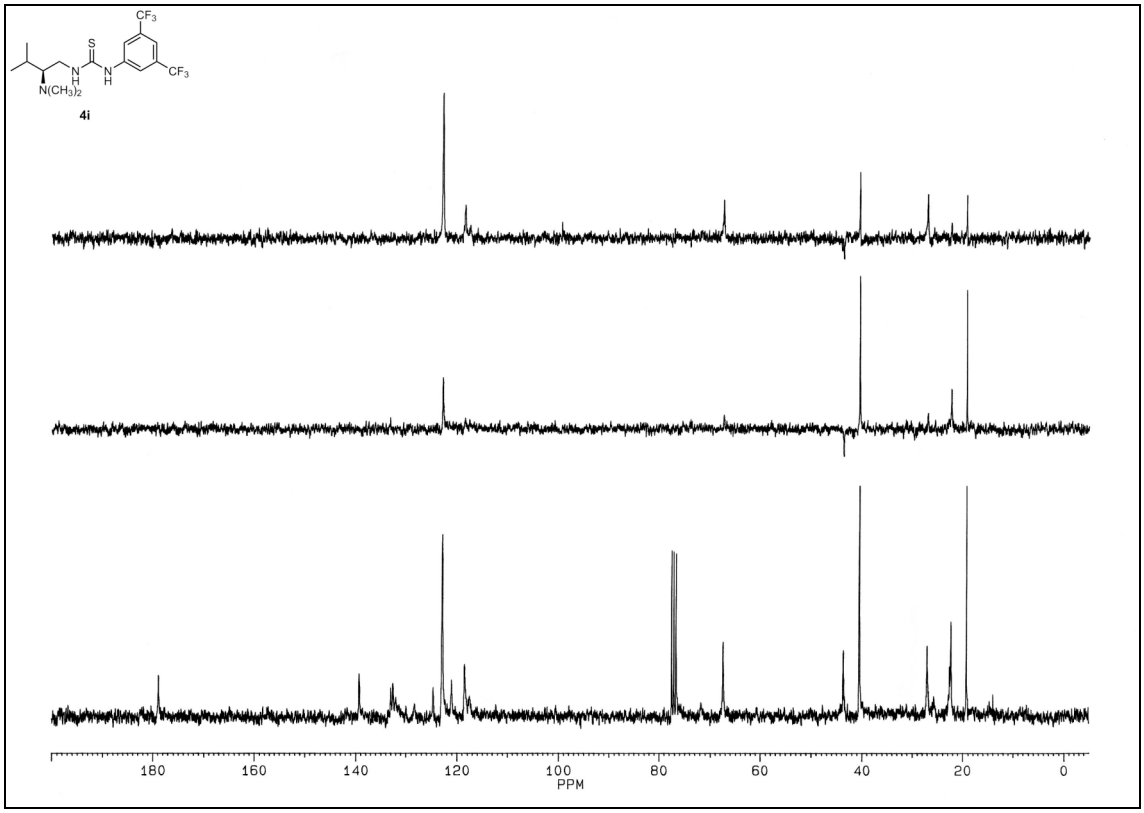

4g
2.018
4.011
.894
.901
.924
1.904
3.075
1.100
3.264
4.235
4.252
PPM


4g
PPM

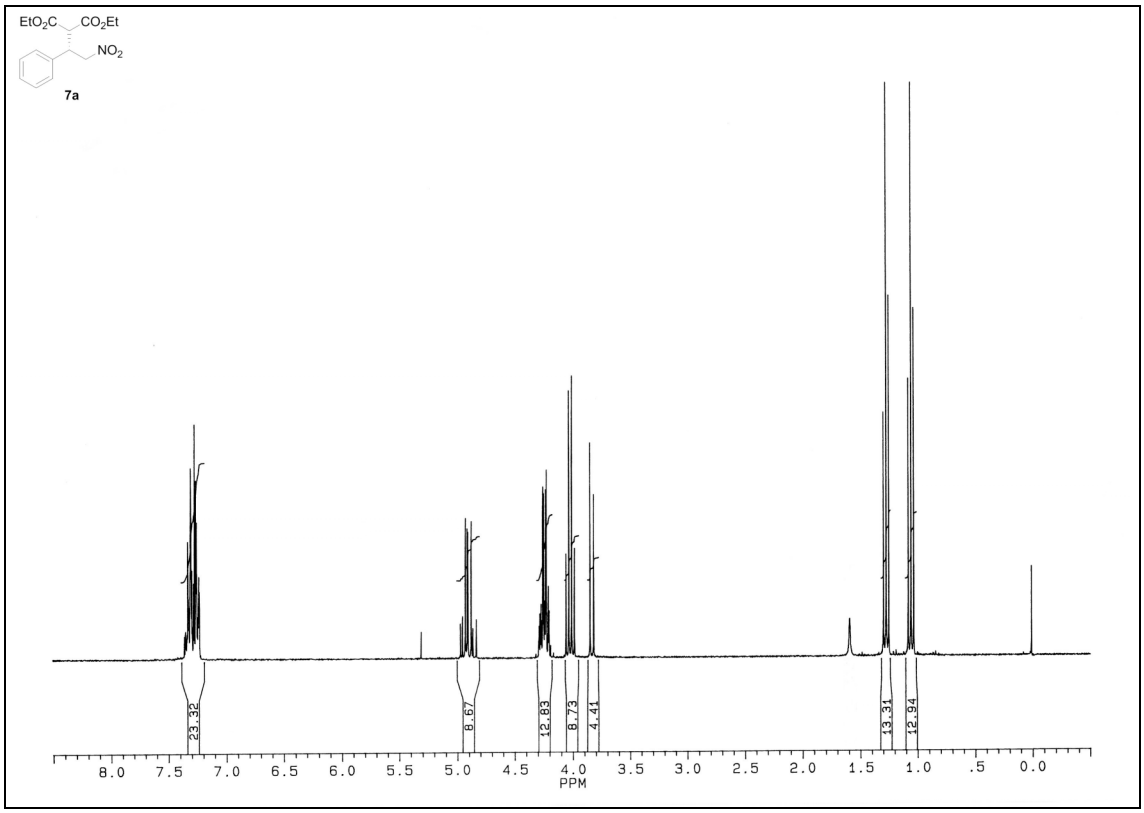

4h
1.887
1.928
1.021
.463
1.125
.413
1.018
6.091
.847
6.093
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5 0.0
PPM

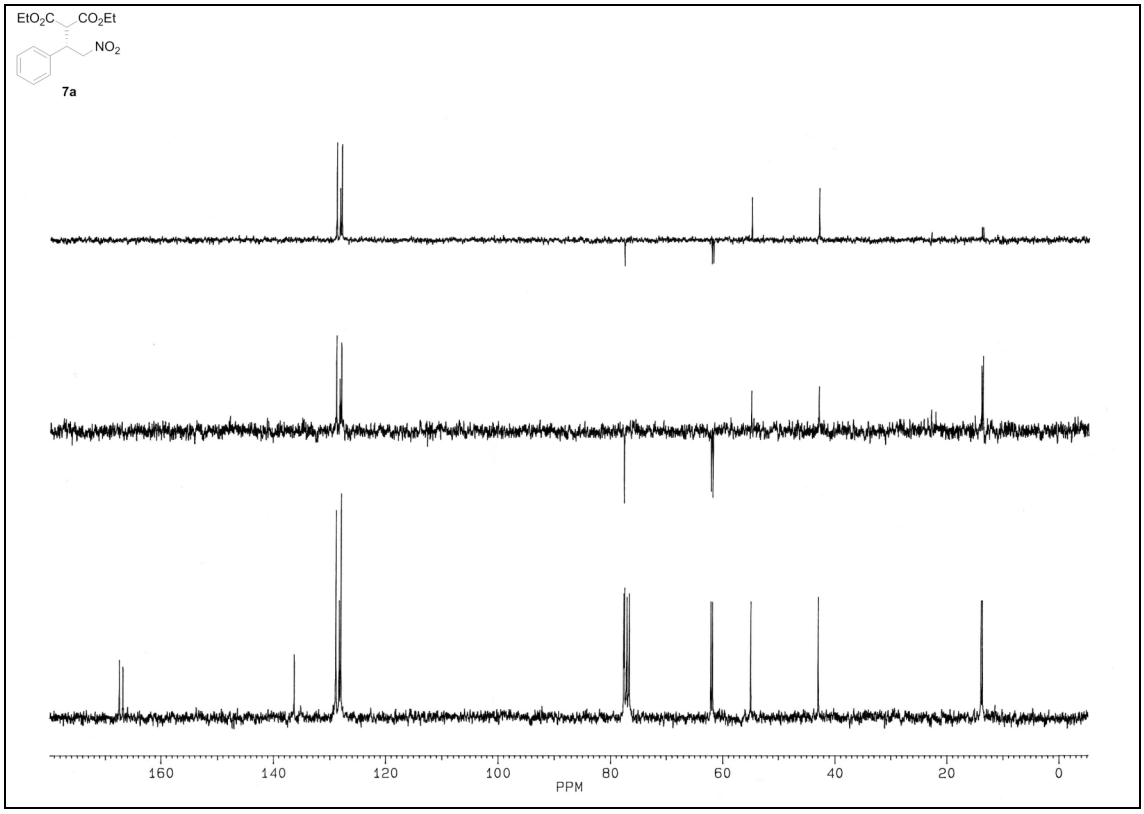

4h
180 160 140 120 100 80 60 40 20 0
PPM

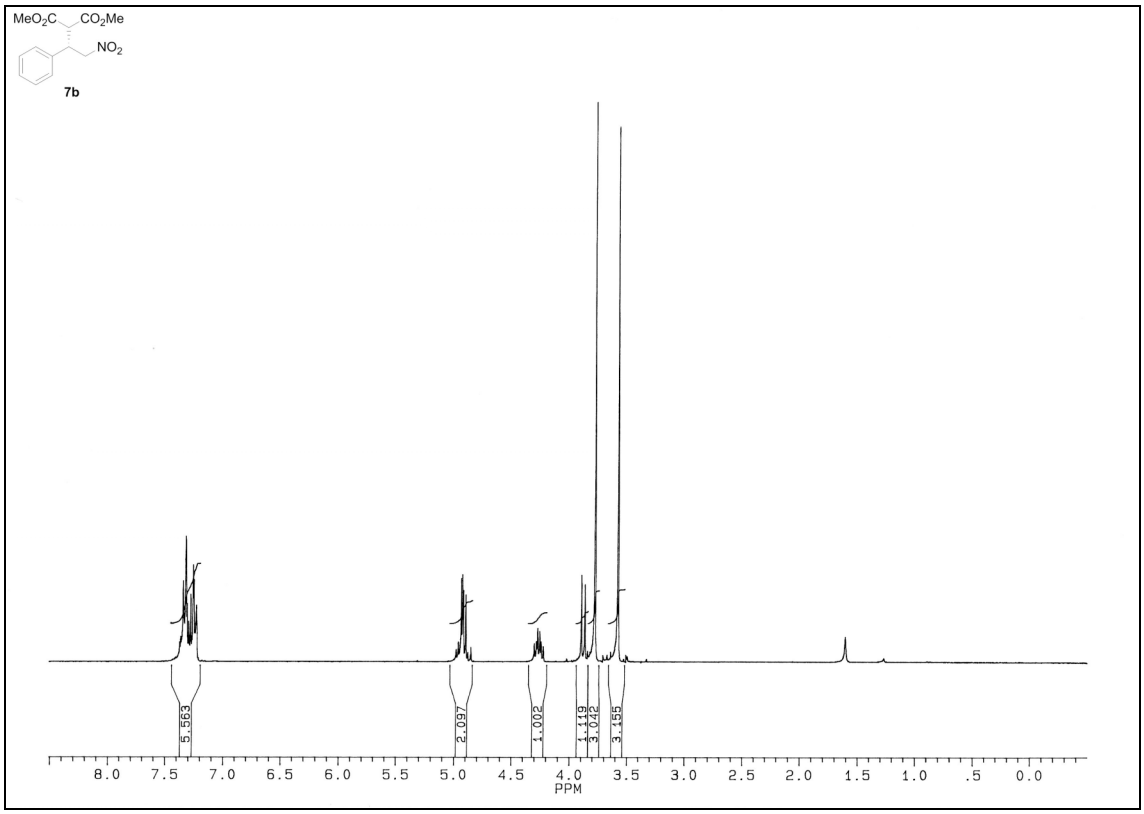

4i
1.997
1.057
.997
.996
6.341
1.030
2.858
2.791
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5 0.0
PPM

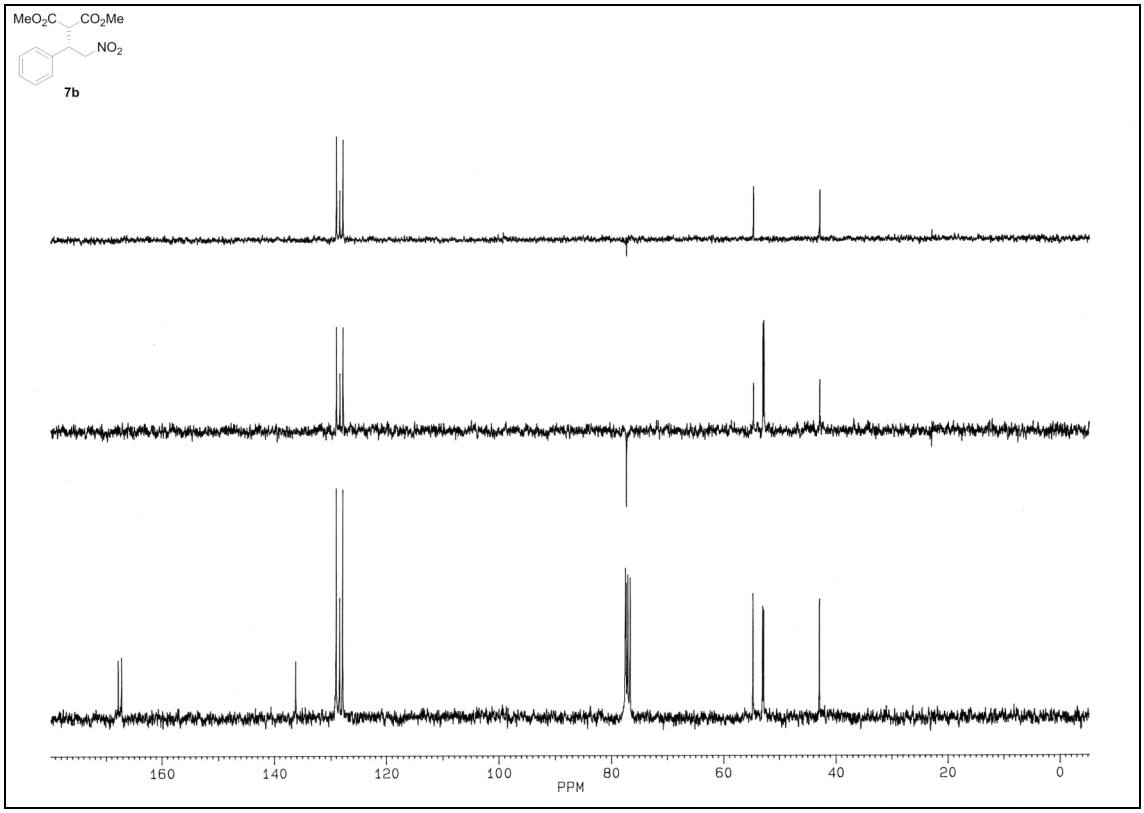

4i
180 160 140 120 100 80 60 40 20 0
PPM

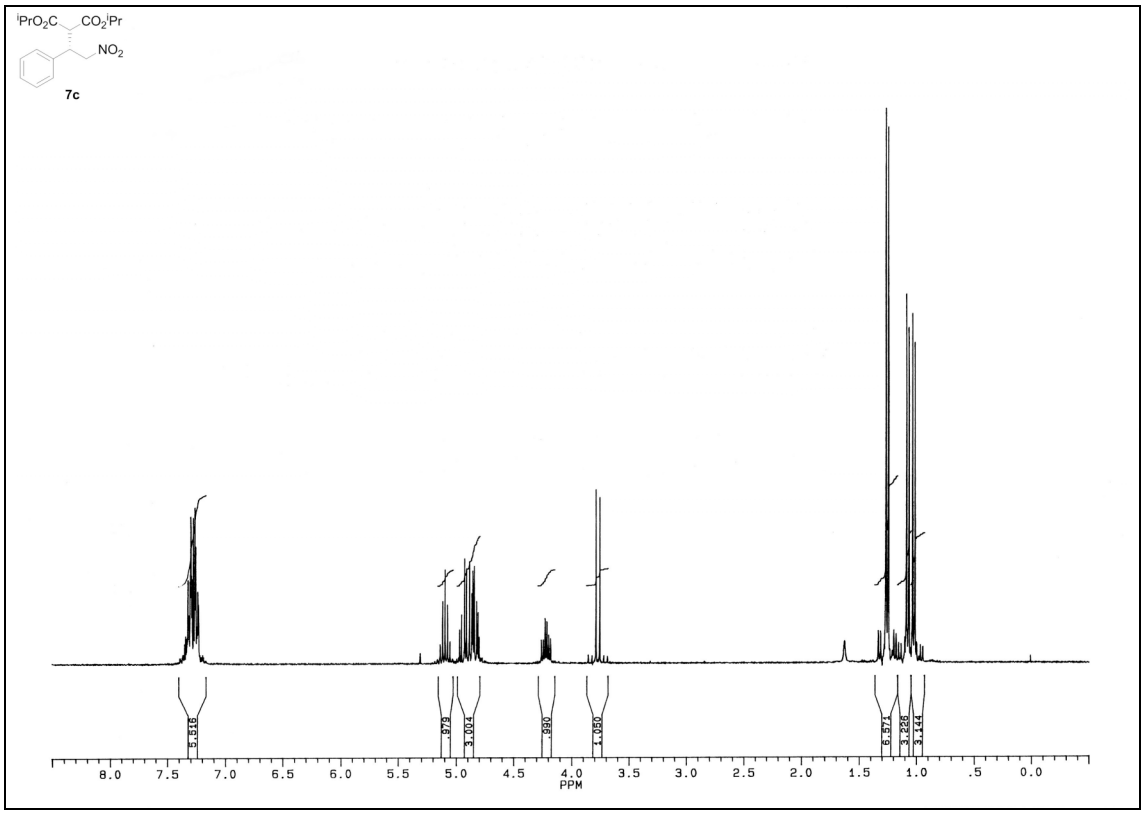
Compounds 7–8

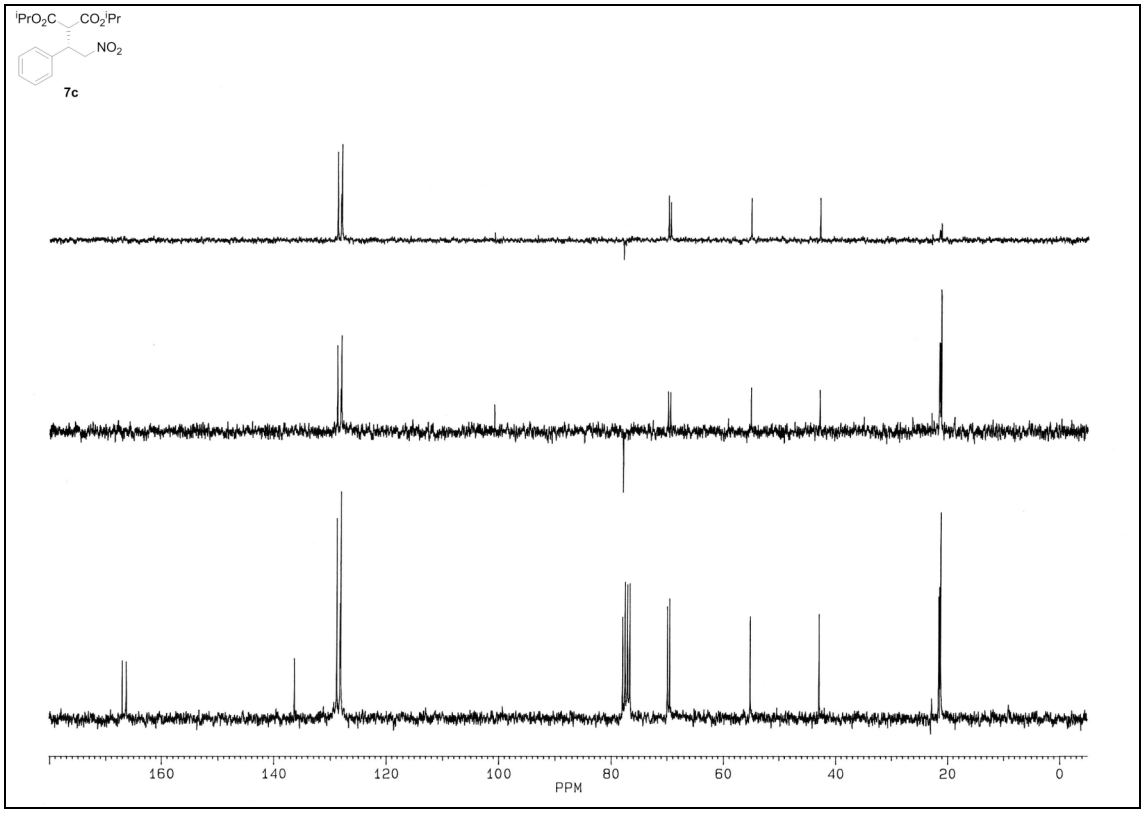


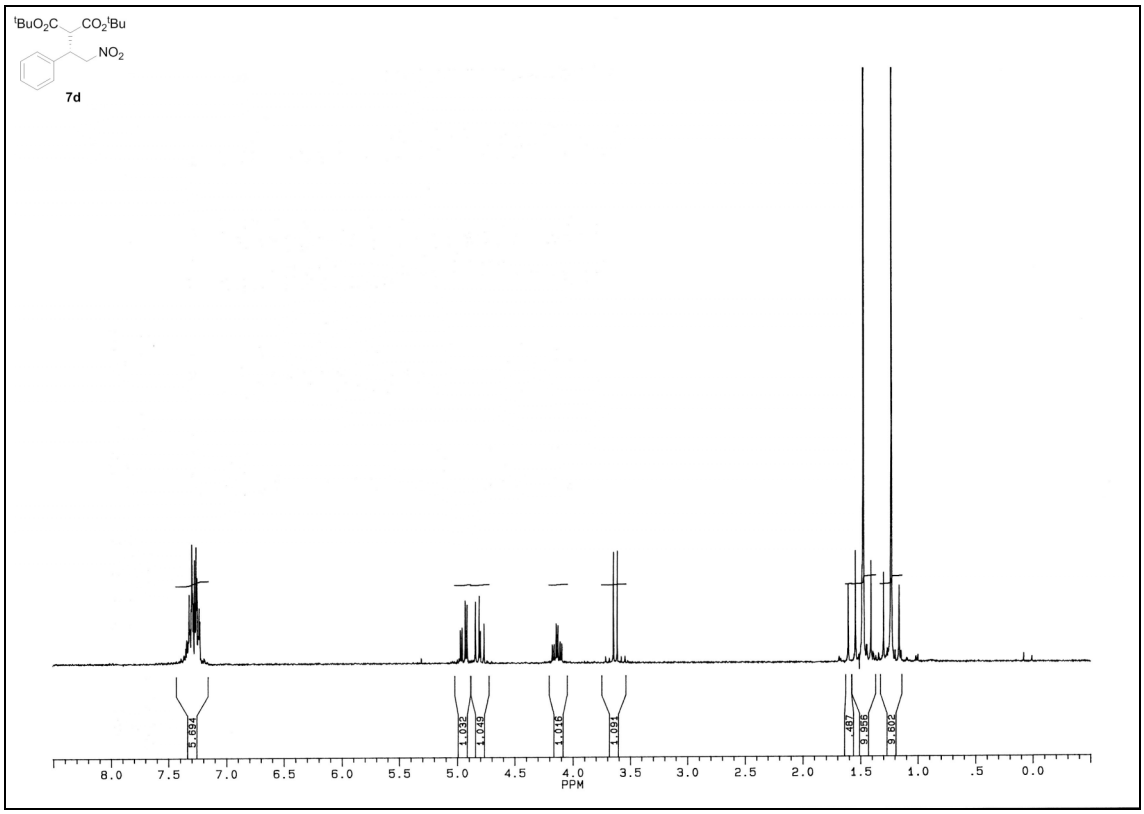


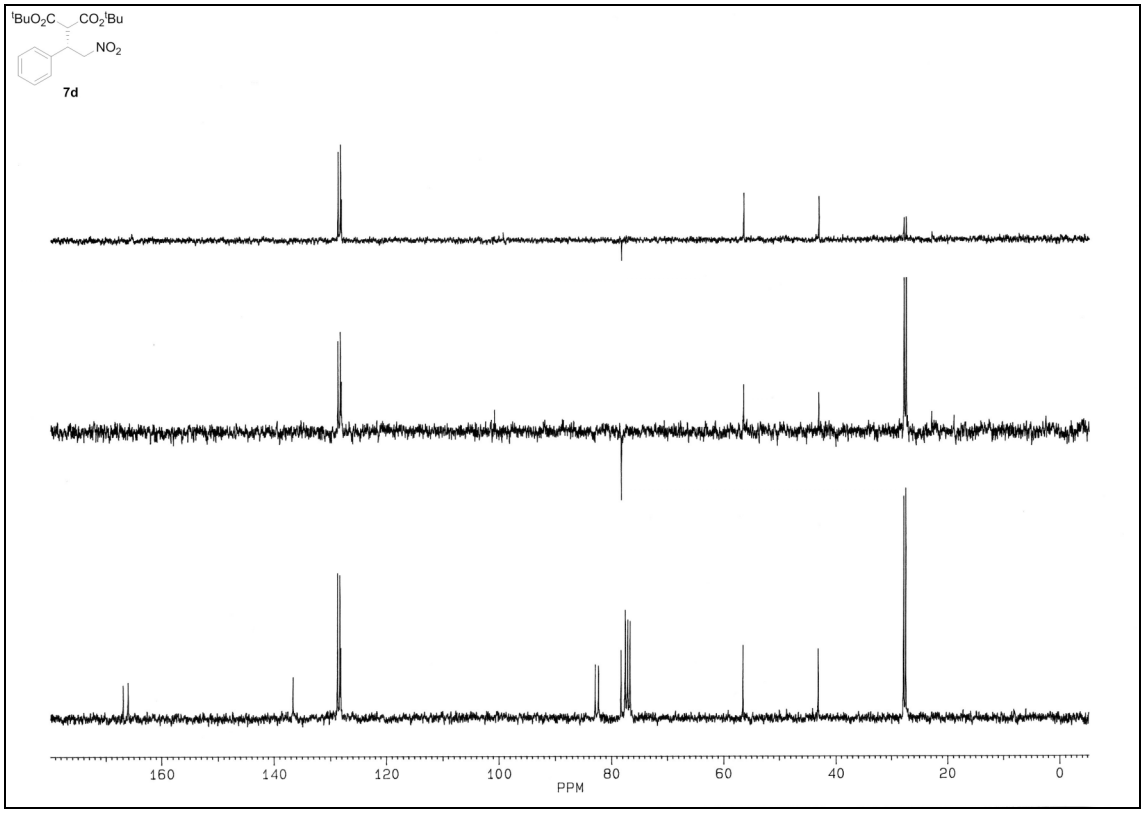

MeO2C
CO2Me
NO2
7b
5.563
2.097
1.002
1.119
3.042
3.155
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5 0.0
PPM

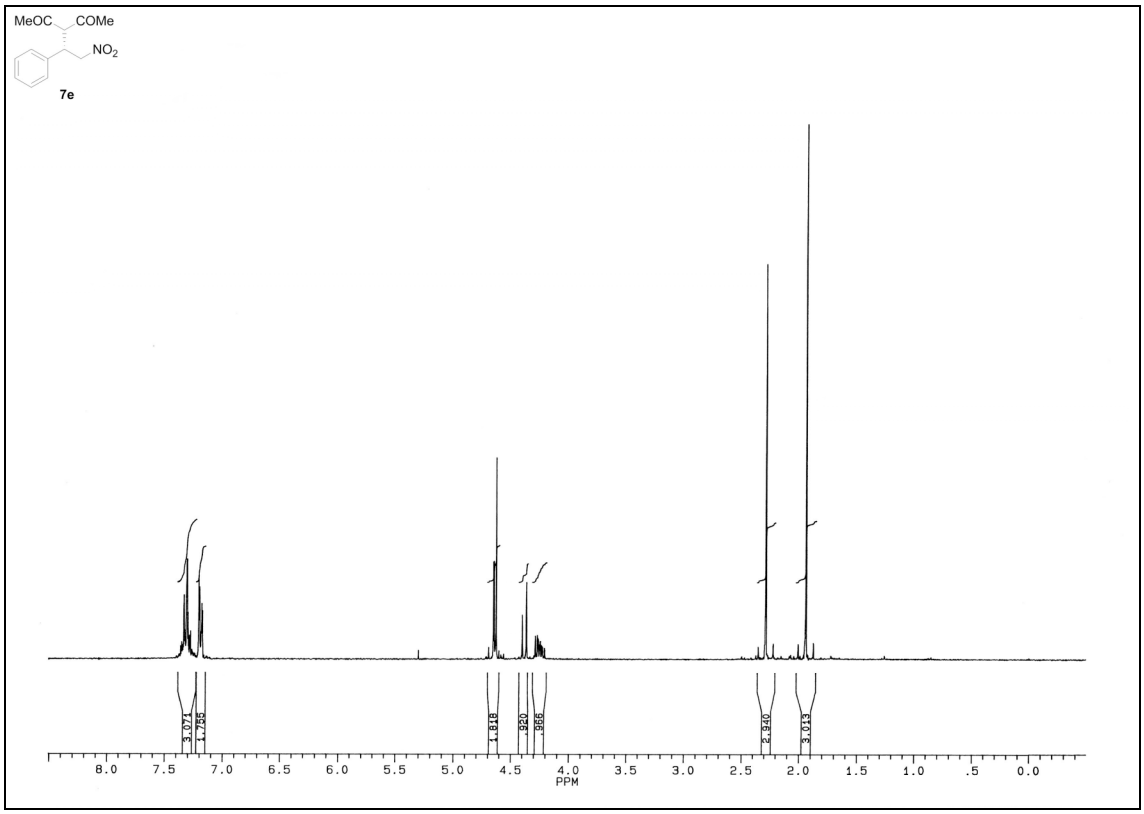

MeO2C
CO2Me
NO2
7b
160 140 120 100 80 60 40 20 0
PPM

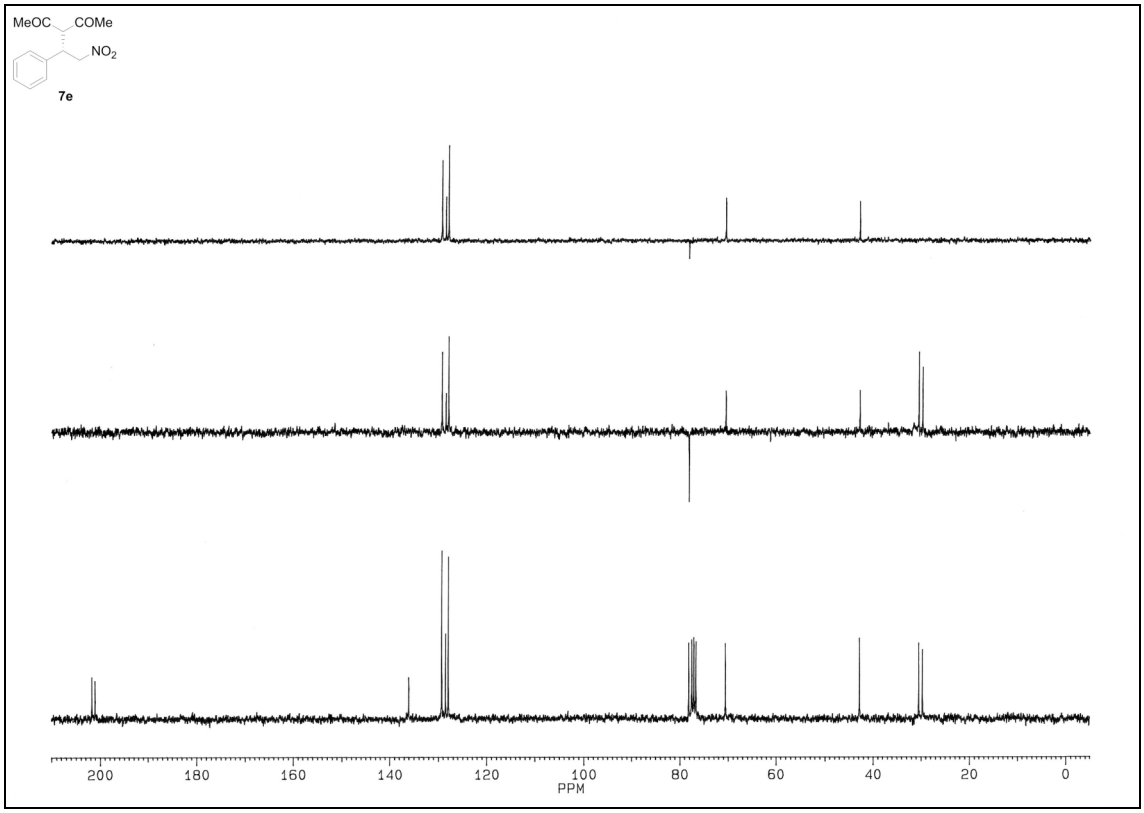

$^{i}PrO_2C$
$CO_2{}^{i}Pr$
NO_2
7c
5.516
.979
3.004
.990
1.050
6.571
3.228
3.144
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
PPM

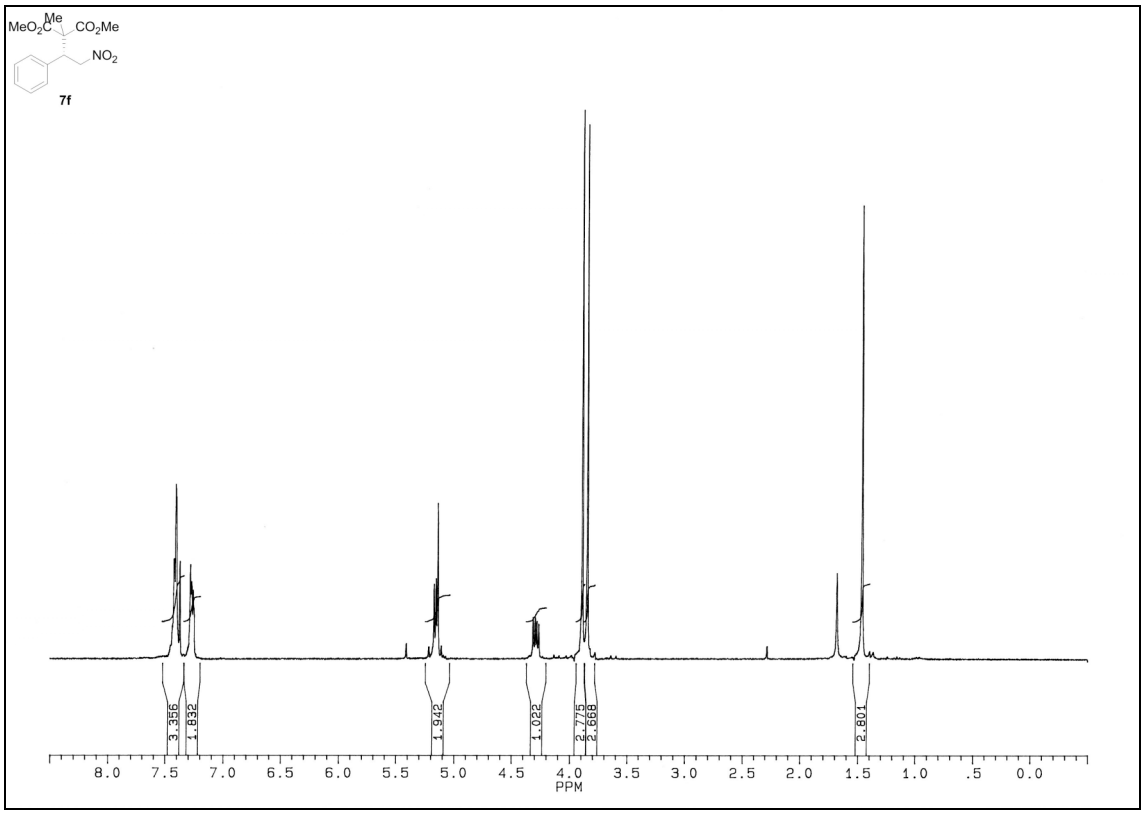

$^{i}PrO_2C$
$CO_2{}^{i}Pr$
NO_2
7c
160
140
120
100
80
60
40
20
0
PPM

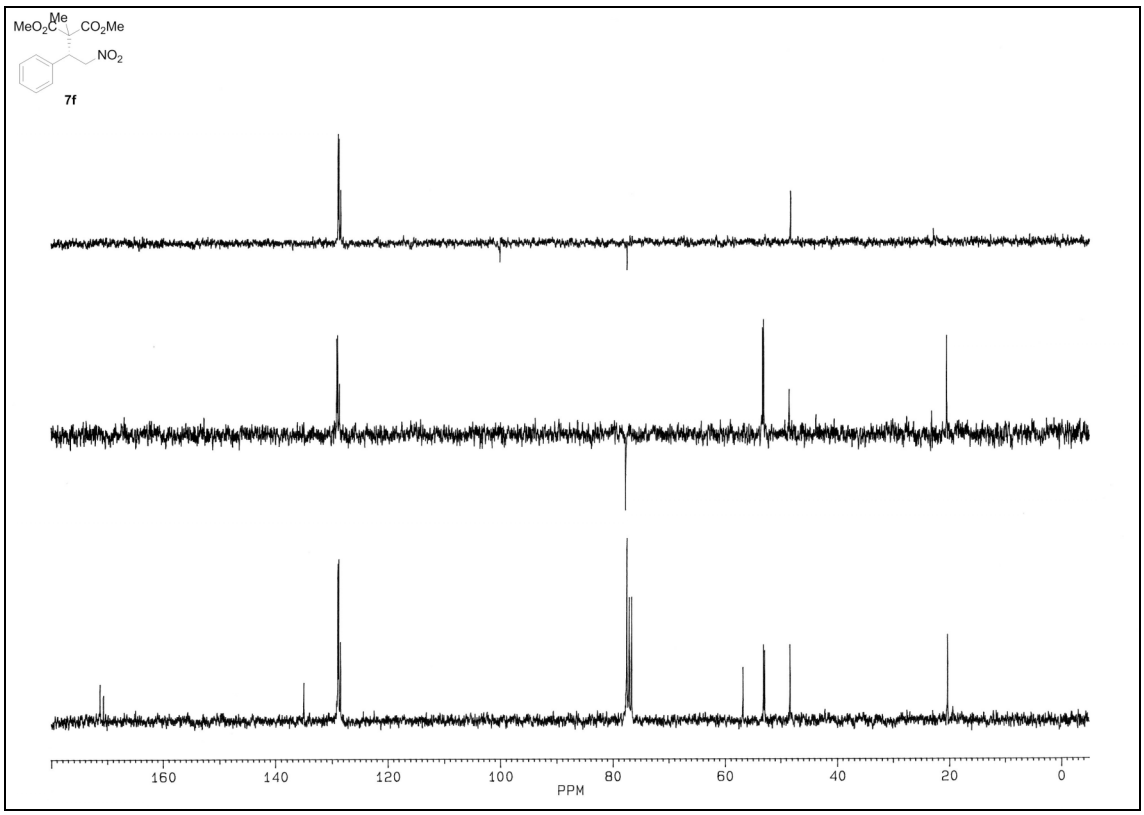

tBuO2C
CO2tBu
NO2
7d
5.694
1.032
1.049
1.016
1.091
.487
9.956
9.602
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
PPM

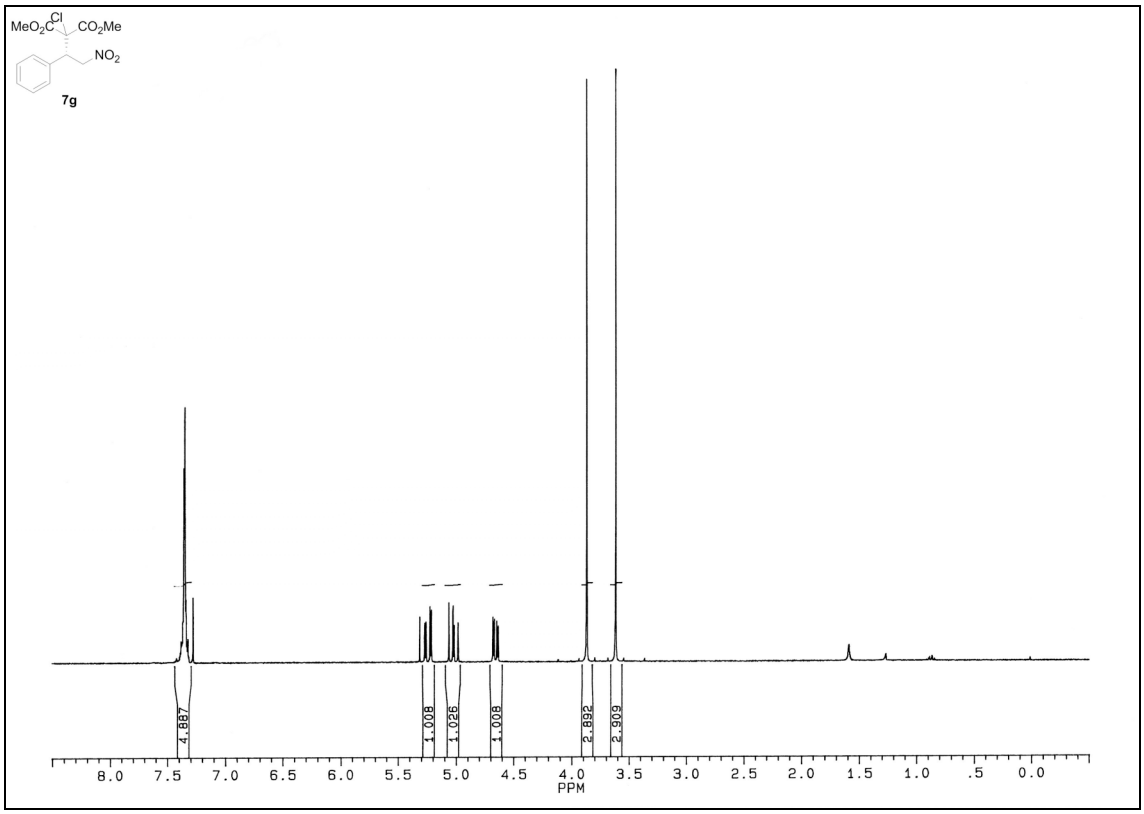

tBuO2C
CO2tBu
NO2
7d
160
140
120
100
80
60
40
20
0
PPM


MeOC
COMe
NO2
7e
3.074
1.755
1.818
.920
.966
2.940
3.013
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
.5
0.0
PPM


MeOC
COMe
NO2
7e
200
180
160
140
120
100
80
60
40
20
0
PPM


MeO2C
Me
CO2Me
NO2
7f
3.356
1.832
1.942
1.022
2.775
2.668
2.801
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 .5 0.0
PPM


MeO2C
Me
CO2Me
NO2
7f
160 140 120 100 80 60 40 20 0
PPM


MeO2C
Cl
CO2Me
NO2
7g
4.887
1.008
1.026
1.008
2.892
2.909
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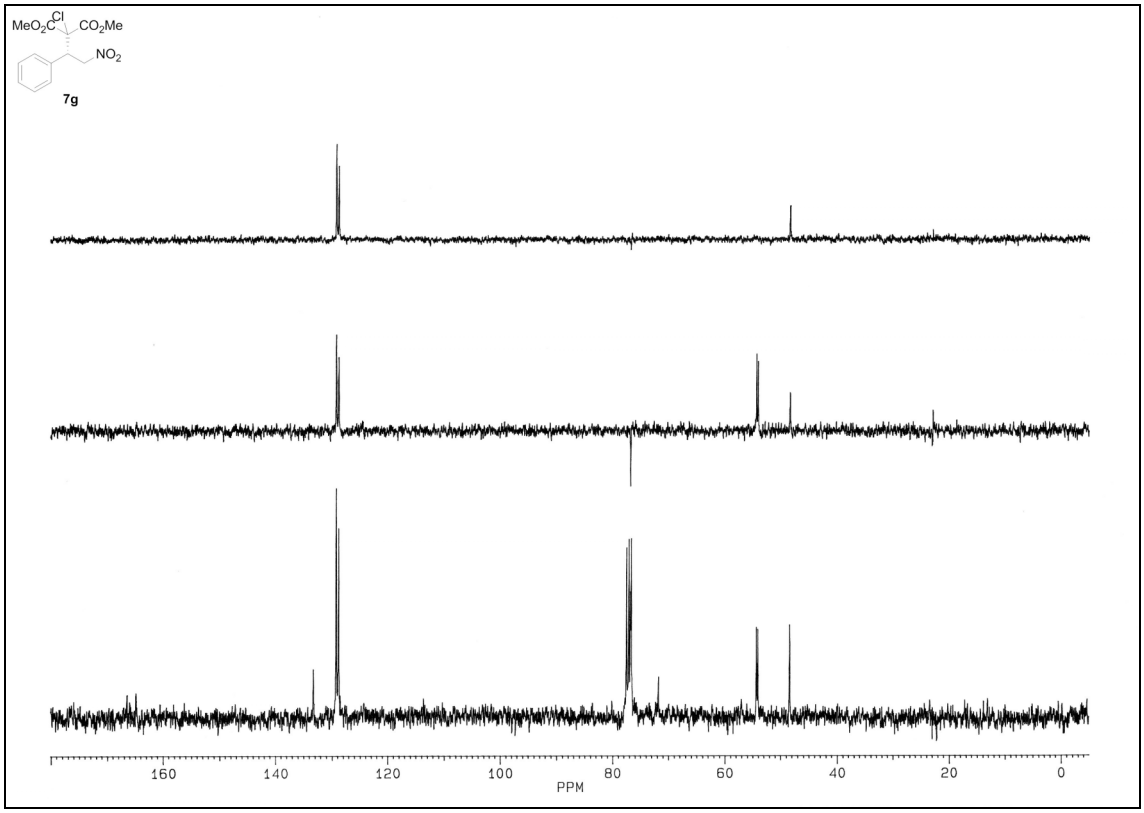
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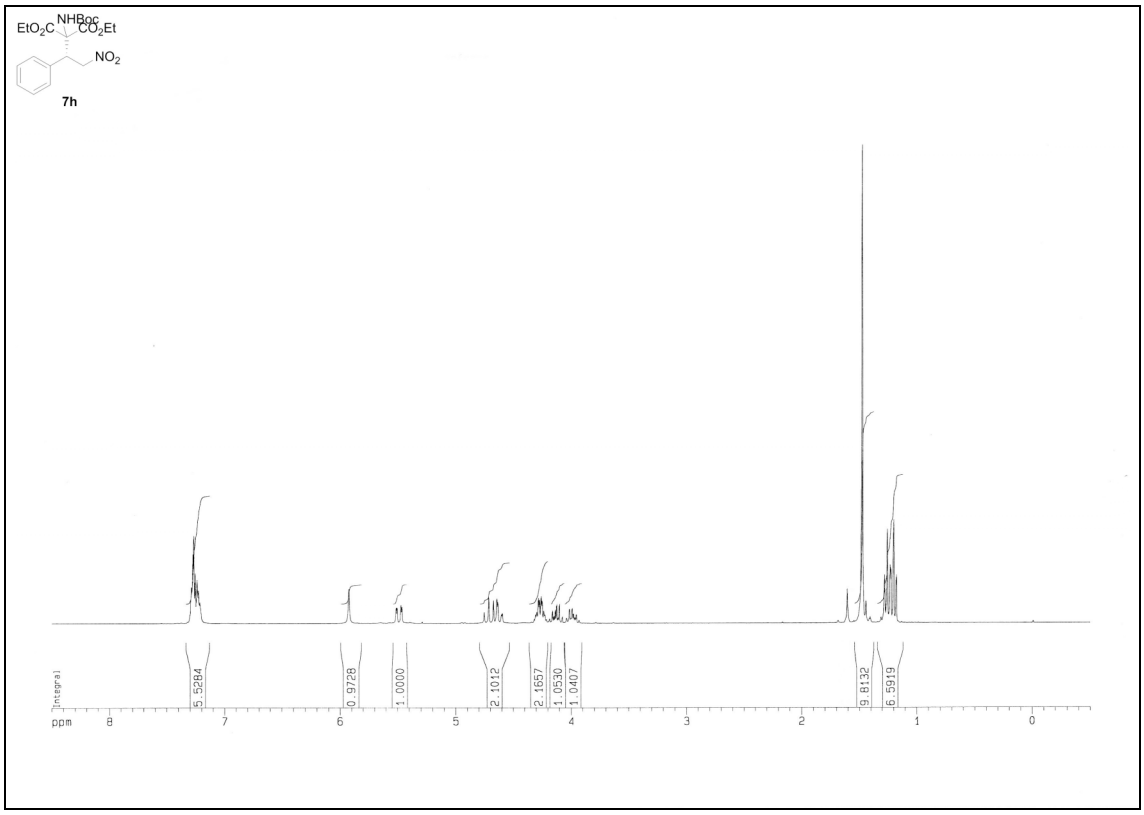
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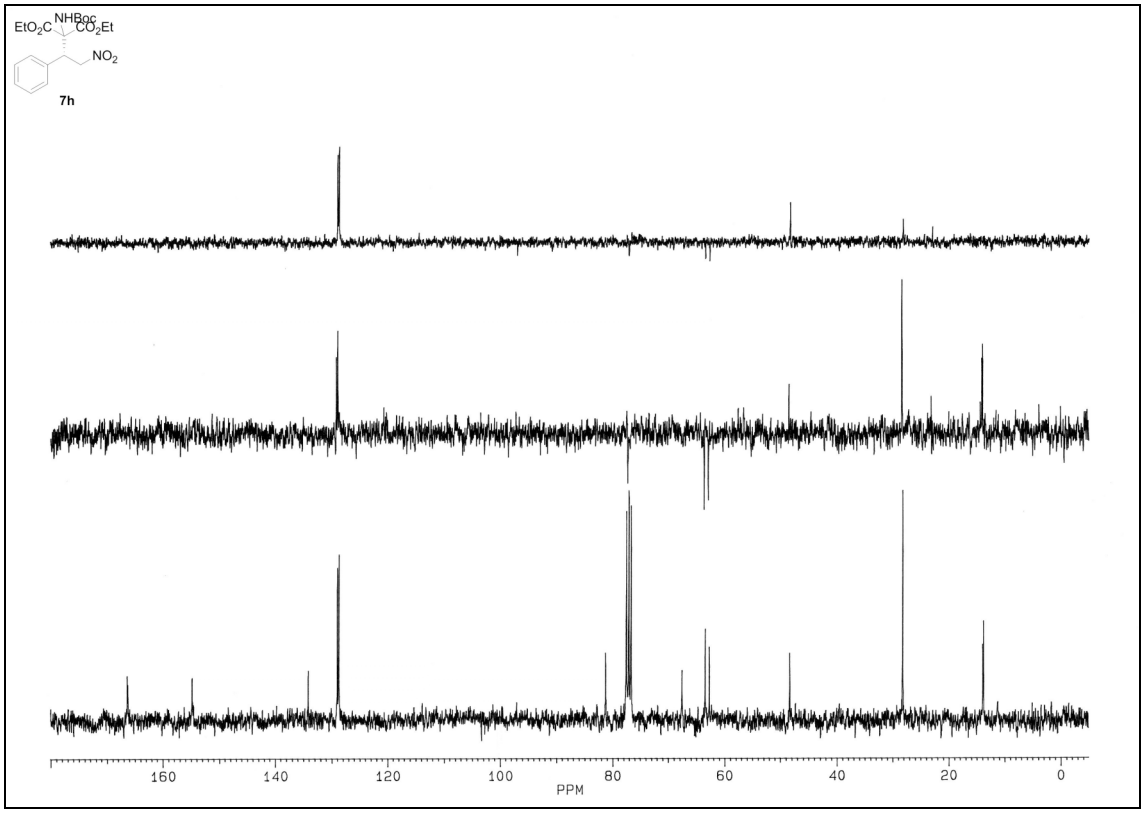
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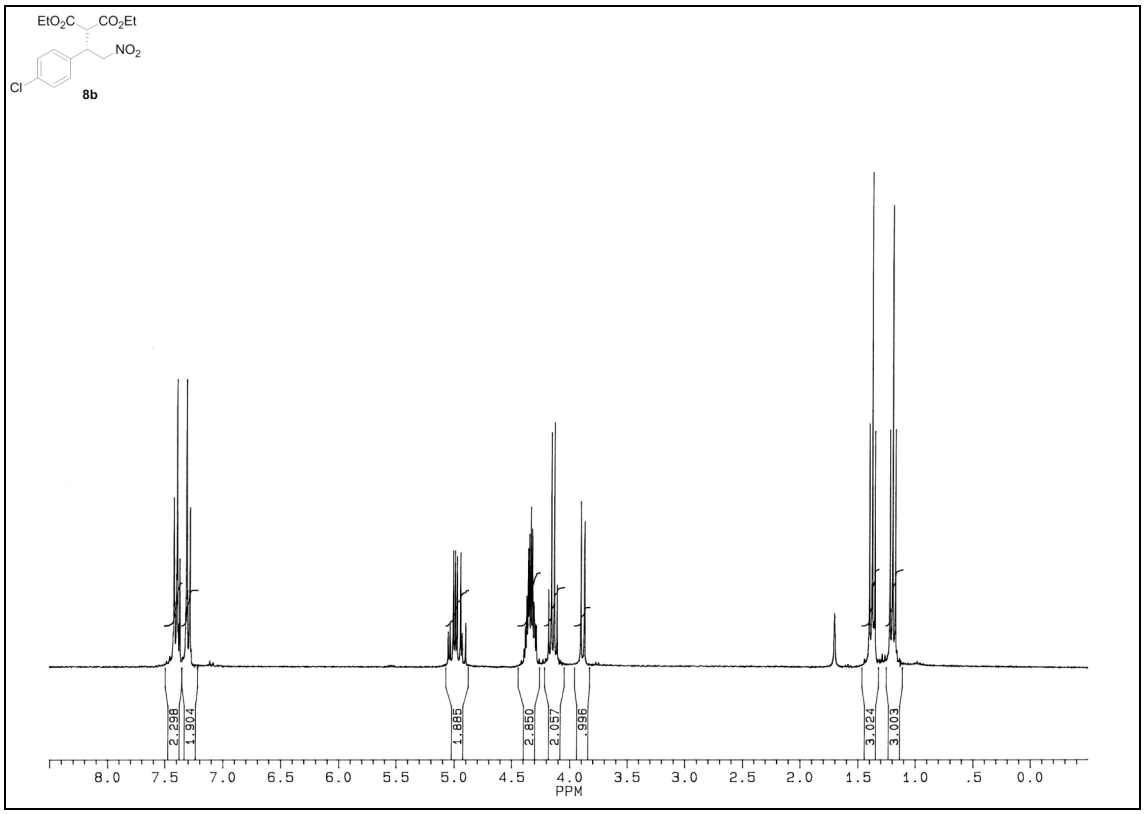
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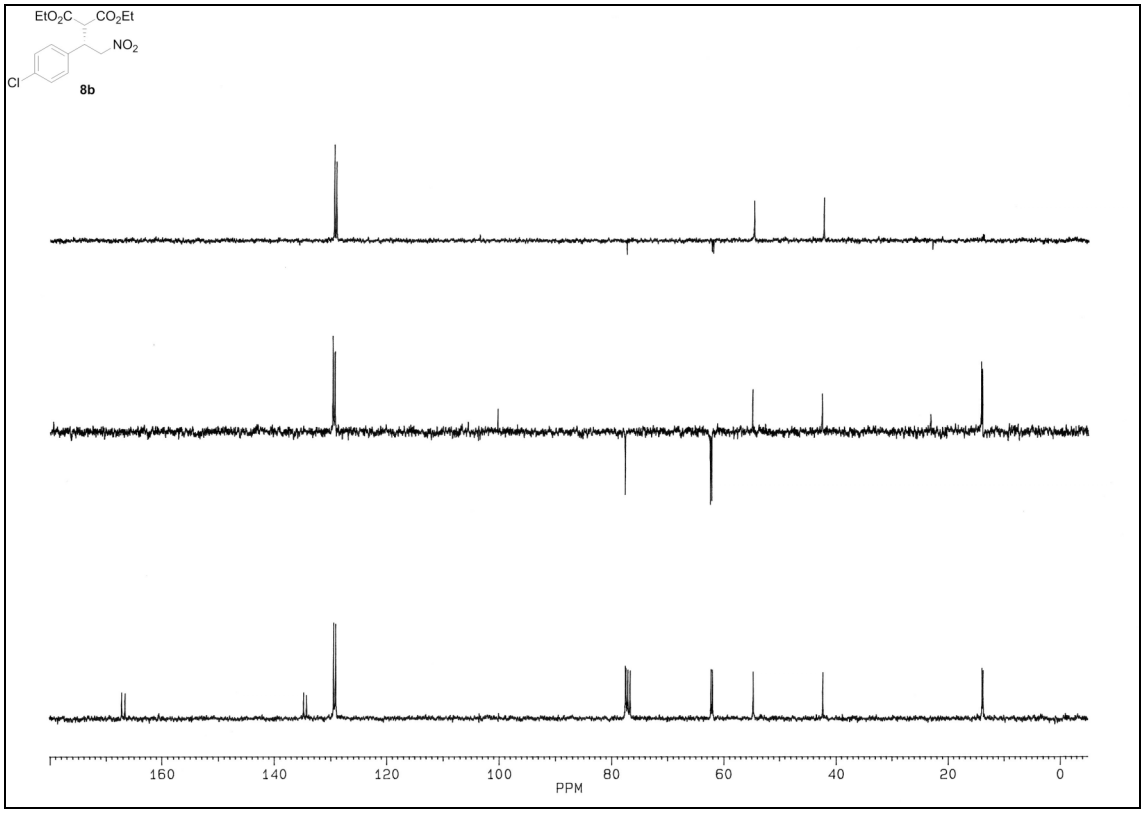
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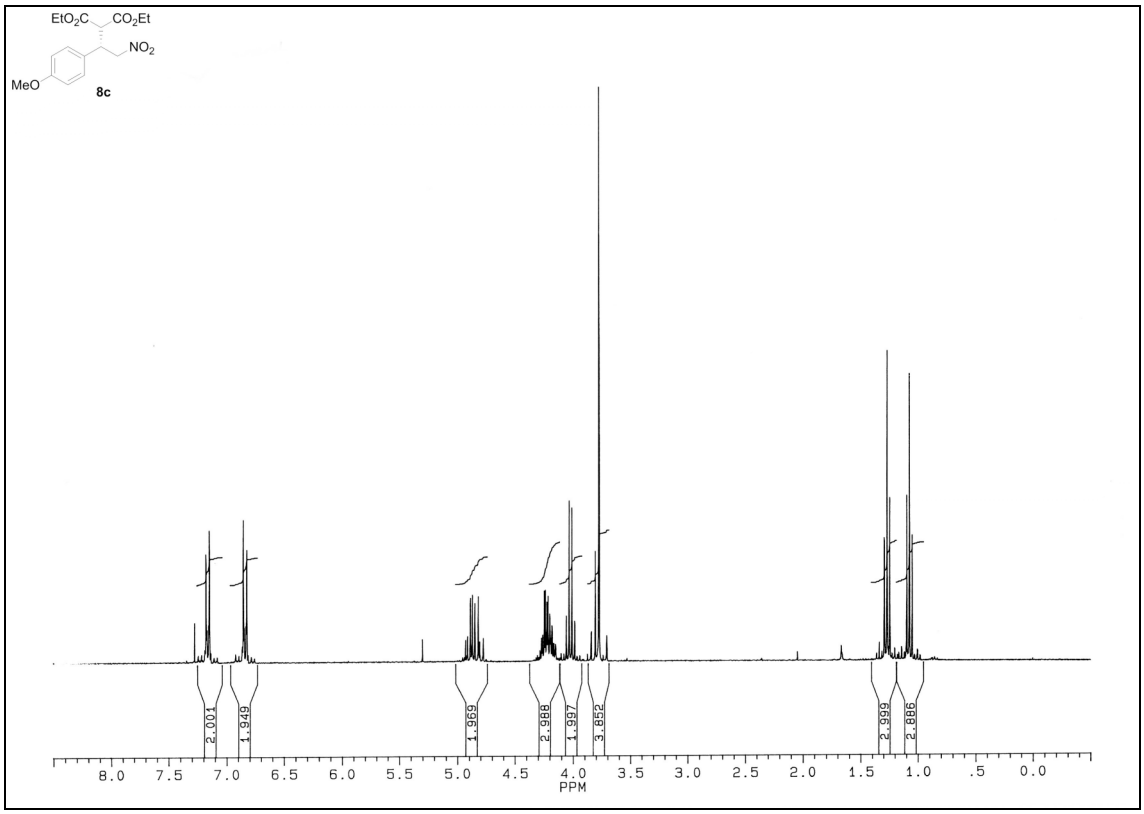
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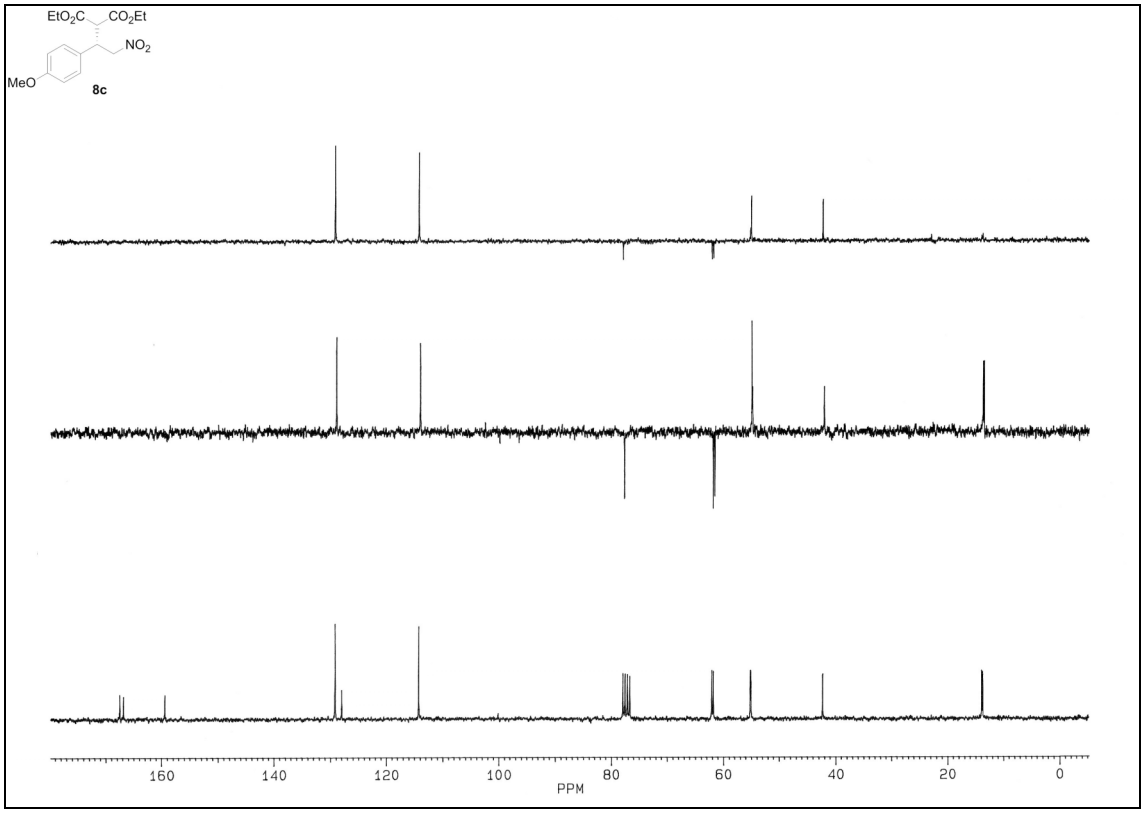
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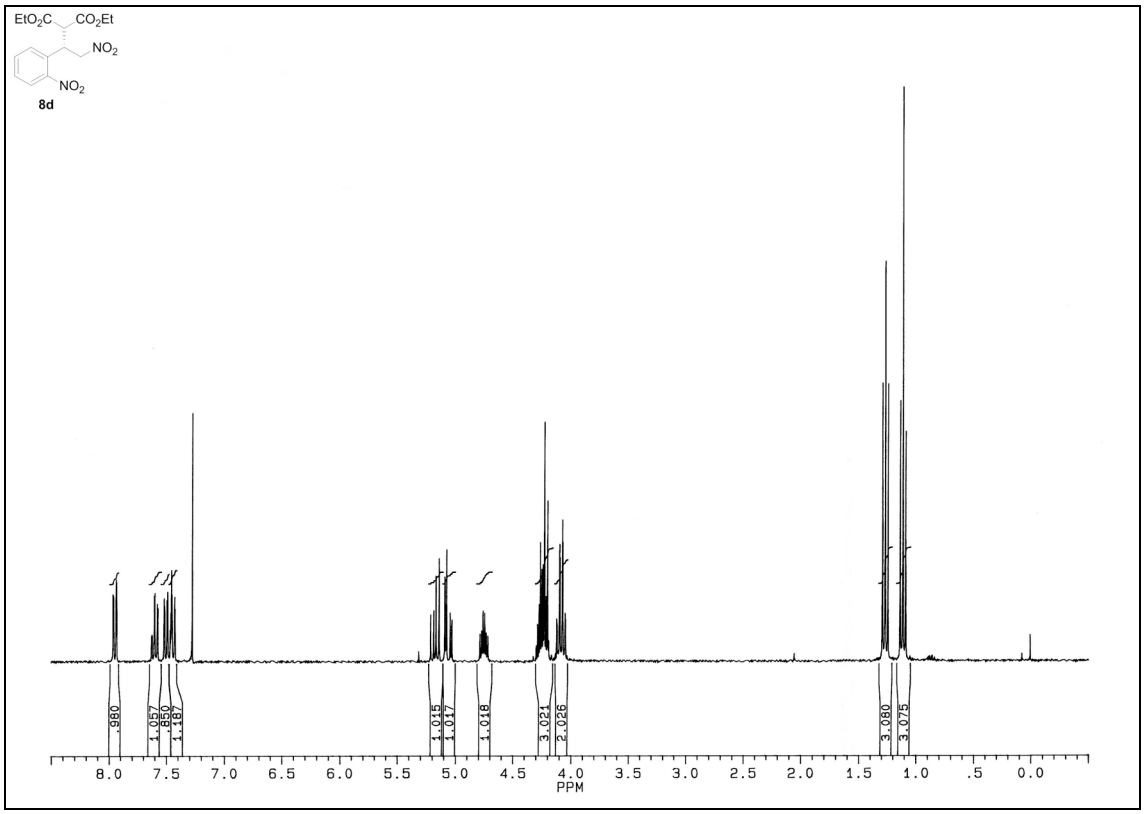
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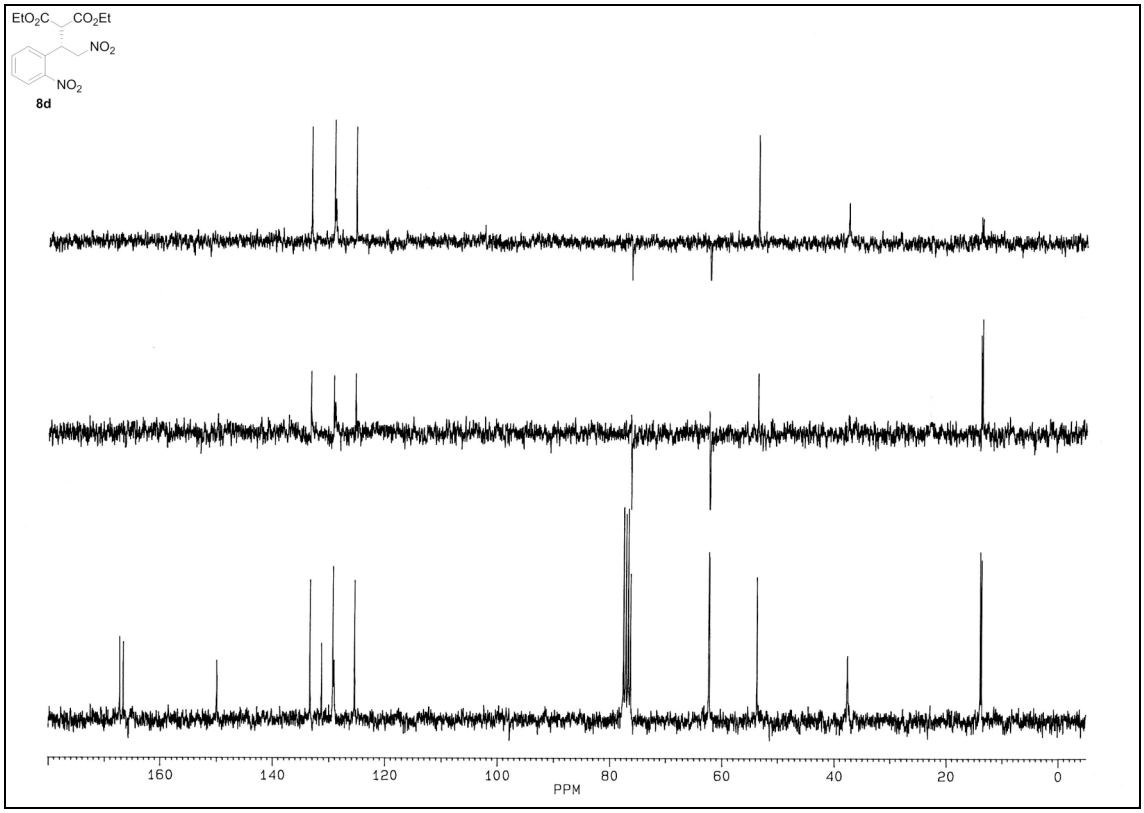
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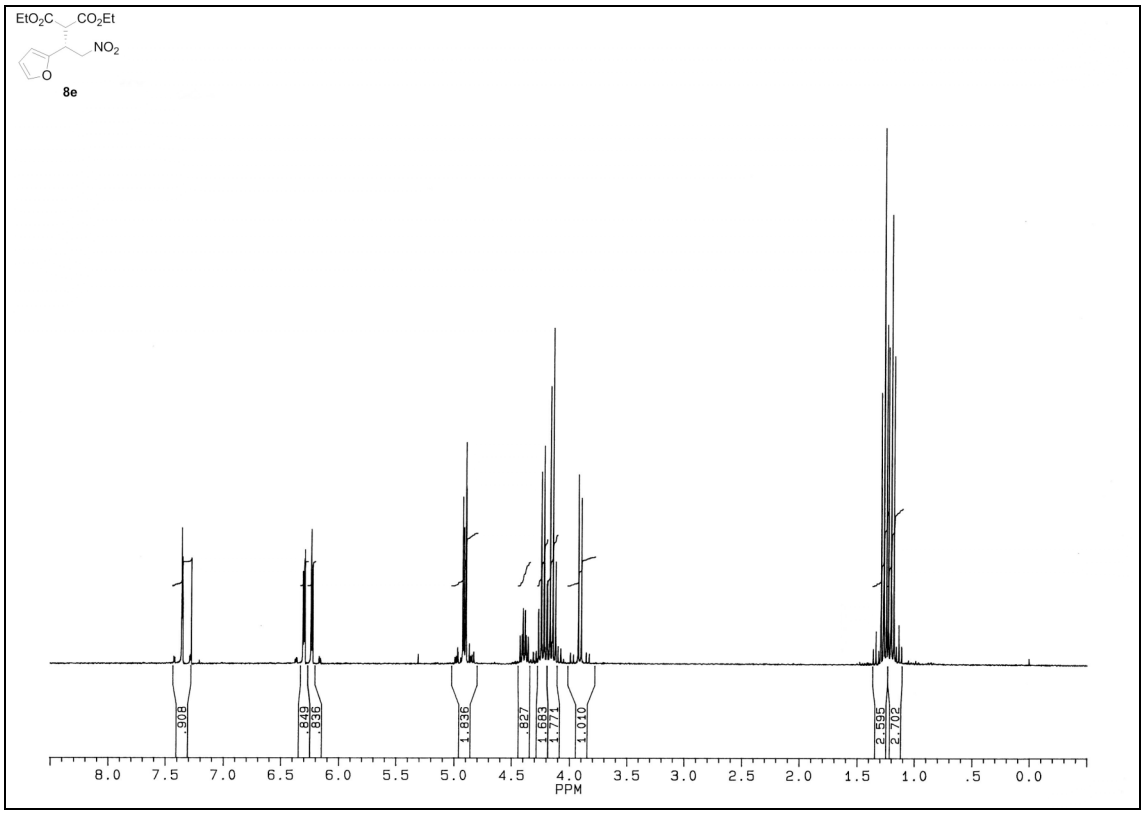
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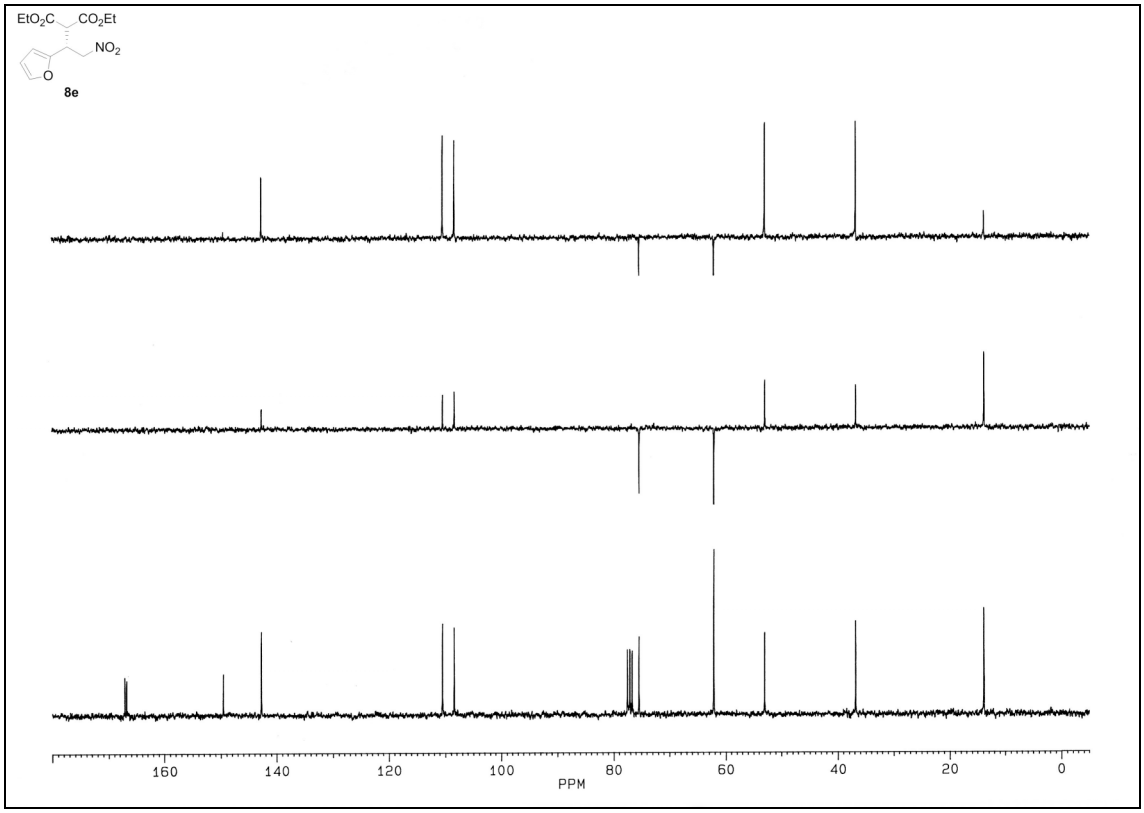
PPM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NO2
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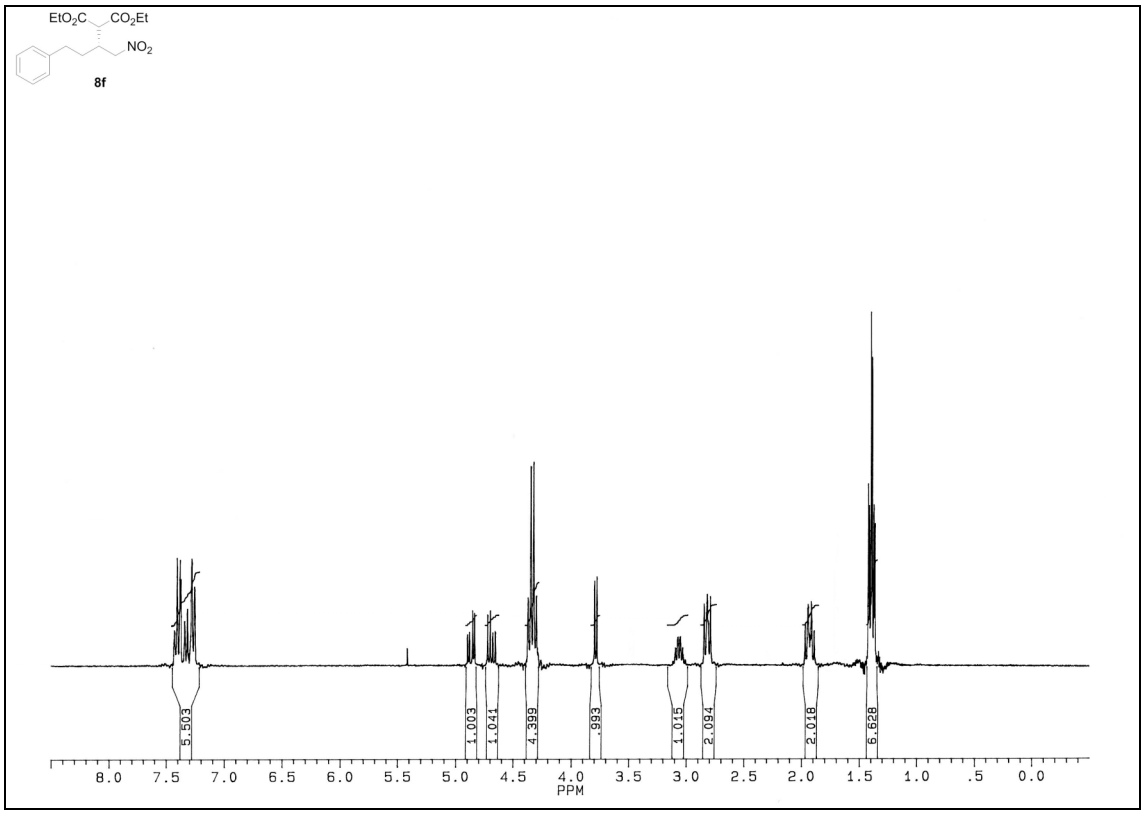
PPM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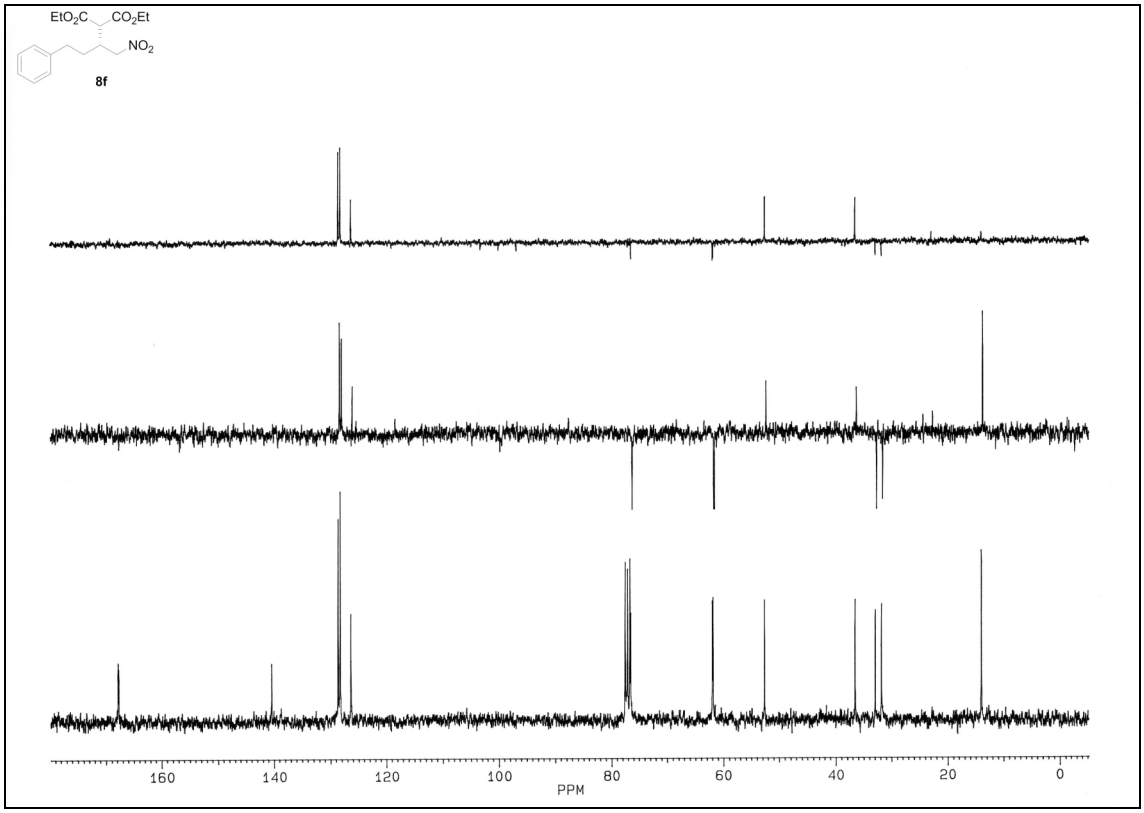
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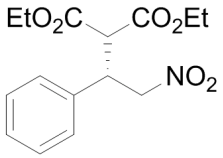
HPLC data



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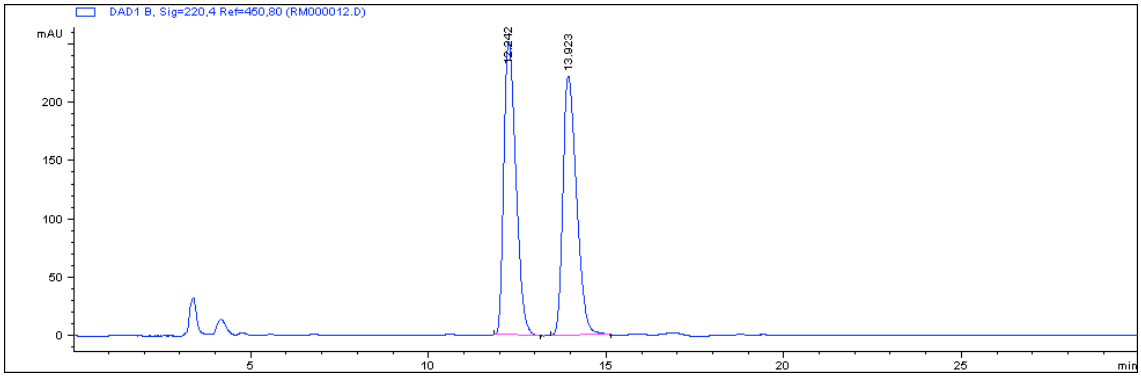
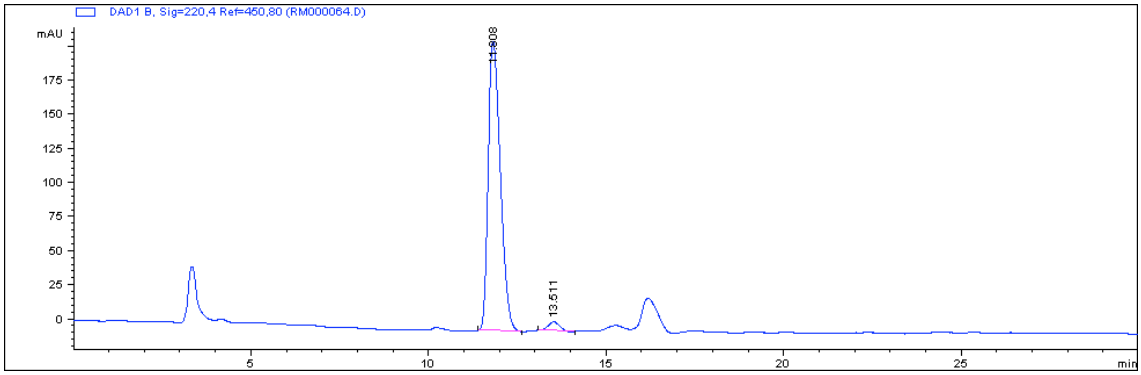
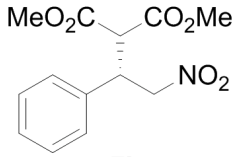


#	Time	Area	Height	Width	Area%	Symmetry
1	12.242	5915.7	252.7	0.3627	49.594	0.628
2	13.923	6012.5	223.1	0.42	50.406	0.632



#	Time	Area	Height	Width	Area%	Symmetry
1	11.808	5082	212.4	0.3752	97.326	0.659
2	13.511	139.6	6.5	0.2665	2.674	0.988



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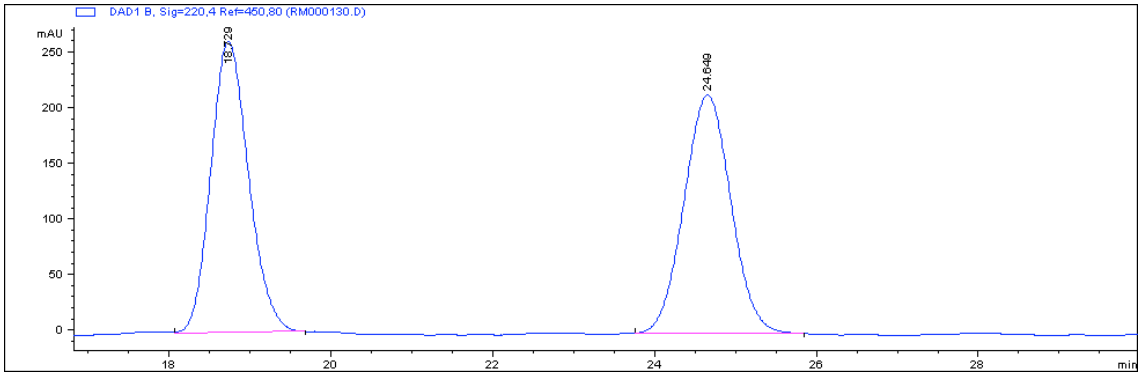
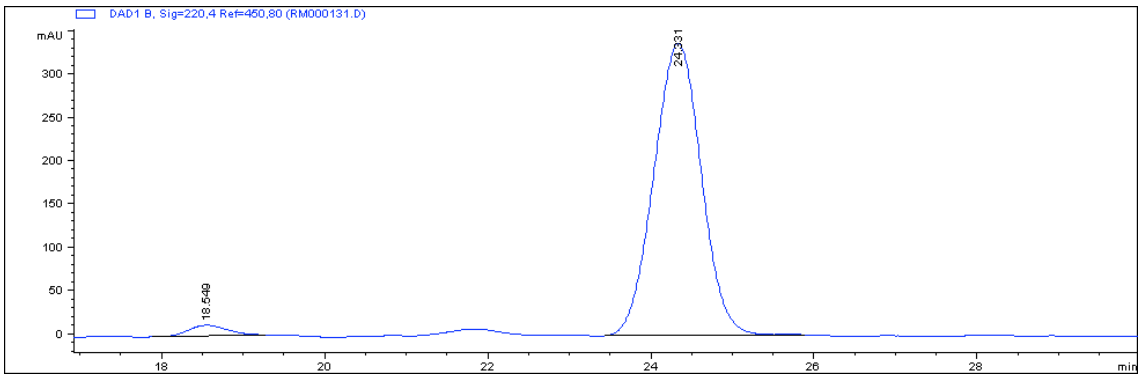
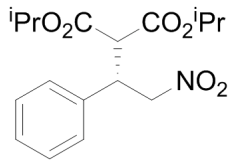


#	Time	Area	Height	Width	Area%	Symmetry
1	18.729	8538.3	262.4	0.5044	49.528	0.845
2	24.649	8701	214.9	0.6195	50.472	0.969



#	Time	Area	Height	Width	Area%	Symmetry
1	18.549	462.4	13	0.5941	3.286	0.791
2	24.331	13608.9	336.9	0.6345	96.714	1.027



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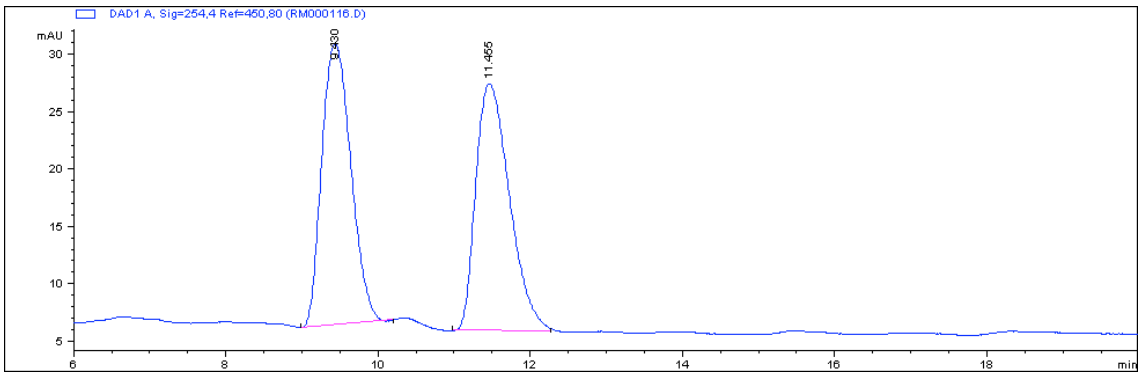
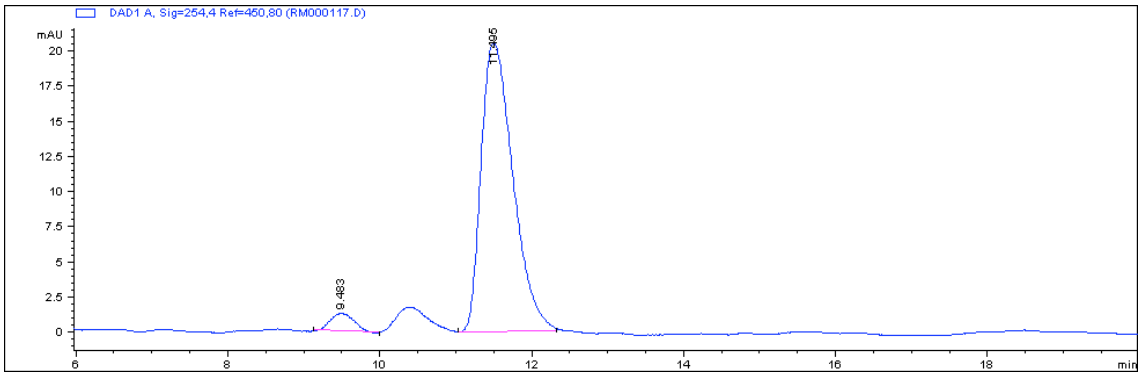
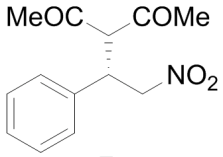


#	Time	Area	Height	Width	Area%	Symmetry
1	9.43	651.6	24.5	0.425	49.533	0.805
2	11.455	663.9	21.5	0.4557	50.467	0.634



#	Time	Area	Height	Width	Area%	Symmetry
1	9.483	27.1	1.3	0.2676	4.334	0.824
2	11.495	598.5	20.6	0.4352	95.666	0.624



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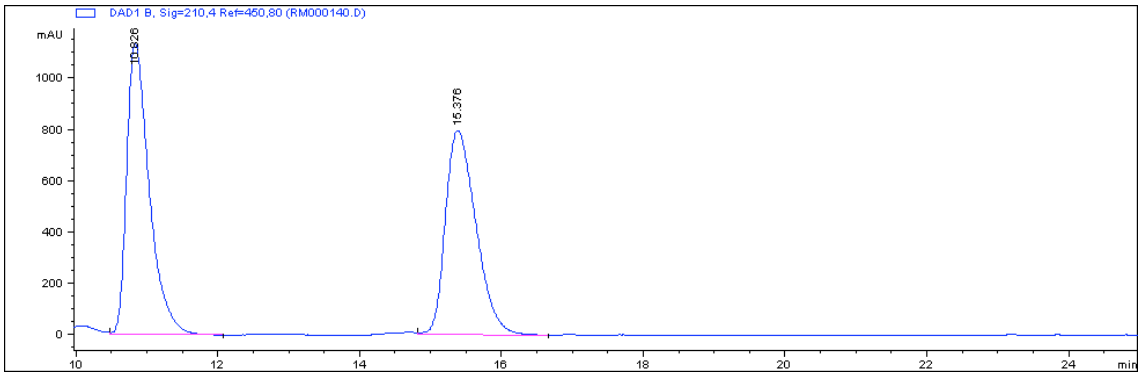
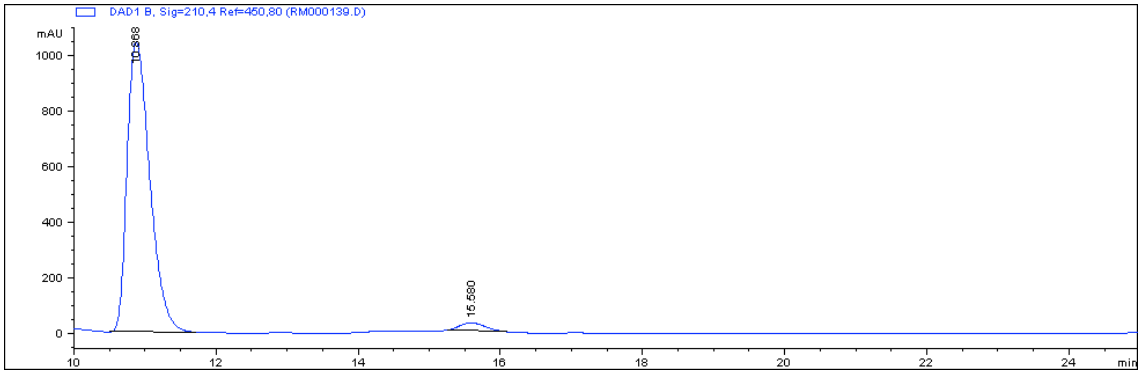
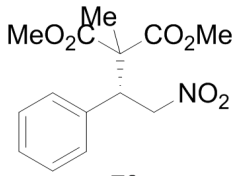


#	Time	Area	Height	Width	Area%	Symmetry
1	10.826	25349.3	1141.5	0.3327	51.346	0.555
2	15.376	24020.2	797.5	0.4442	48.654	0.642



#	Time	Area	Height	Width	Area%	Symmetry
1	10.868	23200.5	1047.3	0.3692	96.702	0.633
2	15.581	791.3	30.9	0.4273	3.298	0.777



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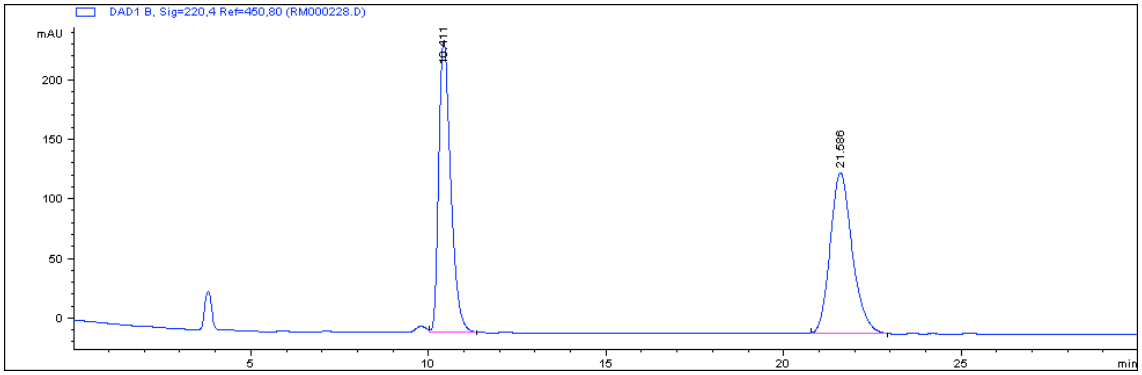
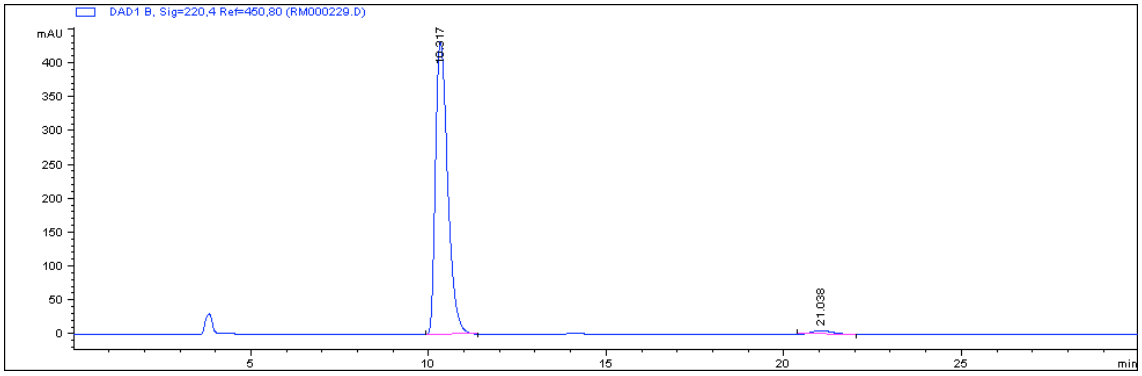
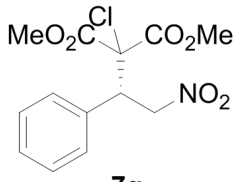


#	Time	Area	Height	Width	Area%	Symmetry
1	10.411	5782.3	244.2	0.369	49.864	0.634
2	21.586	5813.9	135.1	0.6333	50.136	0.819



#	Time	Area	Height	Width	Area%	Symmetry
1	10.317	10354.8	433	0.3718	97.807	0.607
2	21.038	232.1	5.8	0.5101	2.193	0.772



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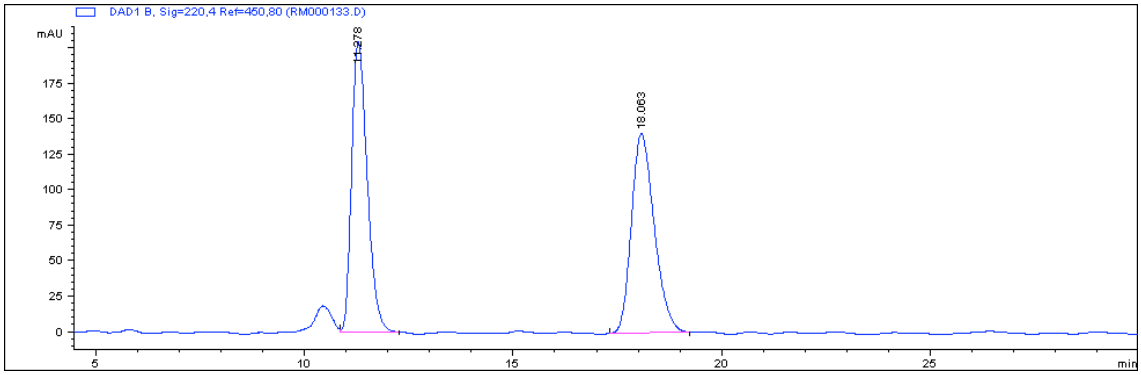
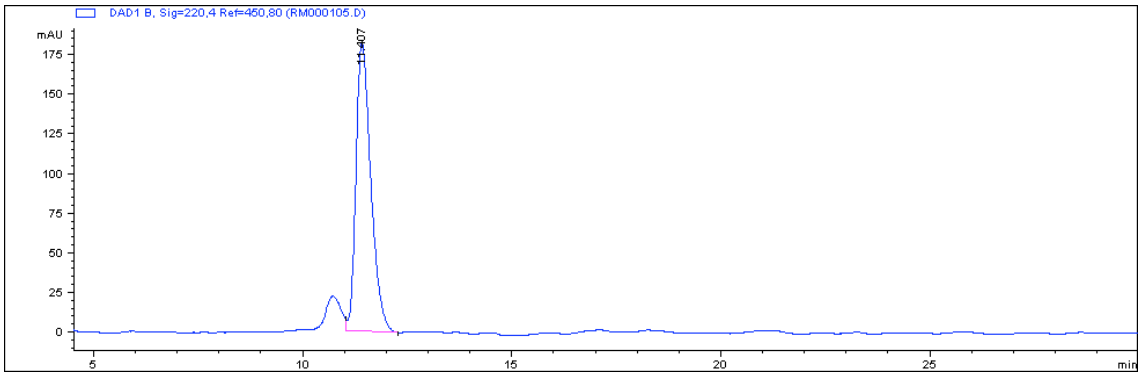
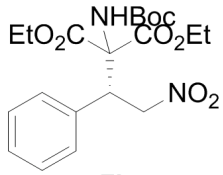


#	Time	Area	Height	Width	Area%	Symmetry
1	11.278	5322.9	204.8	0.4024	49.785	0.69
2	18.063	5368.9	140.5	0.5675	50.215	0.746



#	Time	Area	Height	Width	Area%	Symmetry
1	11.407	4496.5	182.3	0.3773	100.000	0.638



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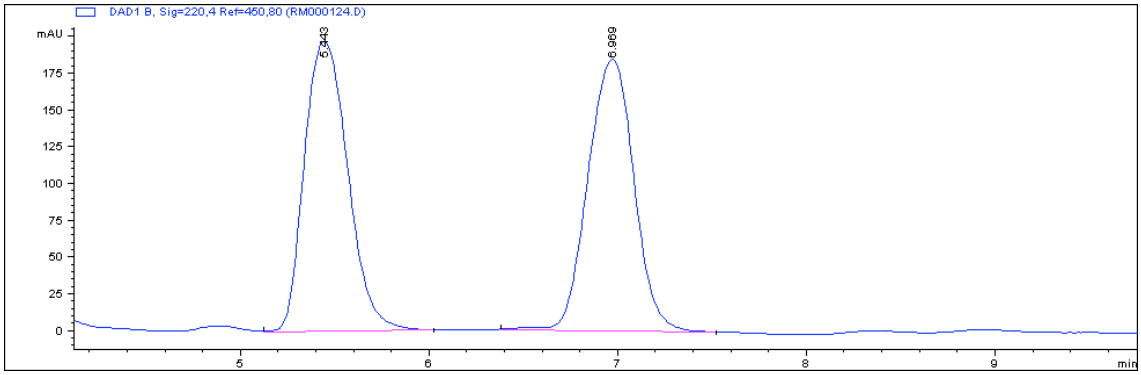
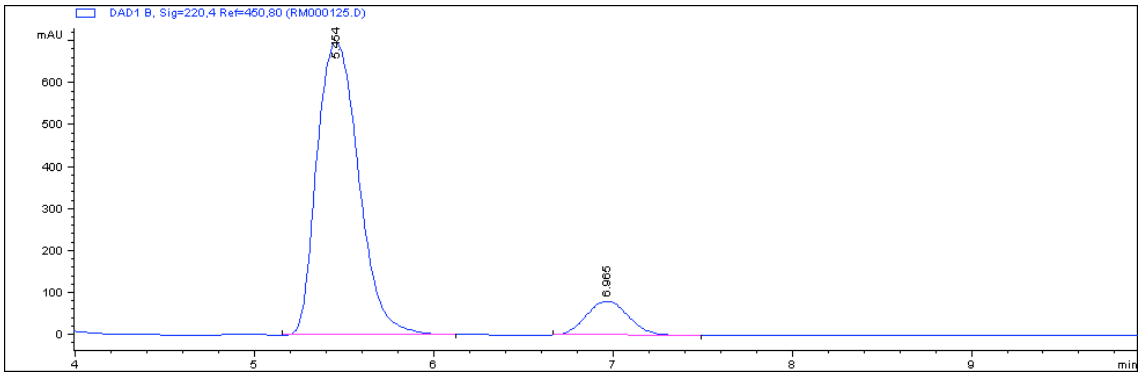
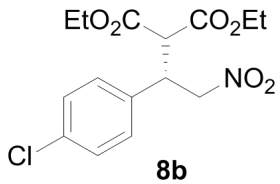


#	Time	Area	Height	Width	Area%	Symmetry
1	5.443	3172.1	197.6	0.2609	50.240	0.81
2	6.969	3141.8	185	0.2718	49.760	1.079



#	Time	Area	Height	Width	Area%	Symmetry
1	5.454	11286	697.7	0.2591	89.539	0.787
2	6.965	1318.5	80.7	0.261	10.461	0.912



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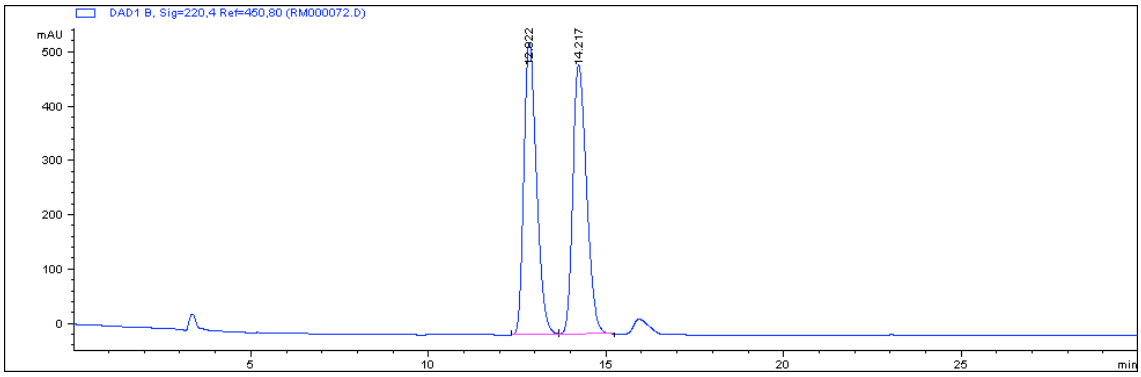
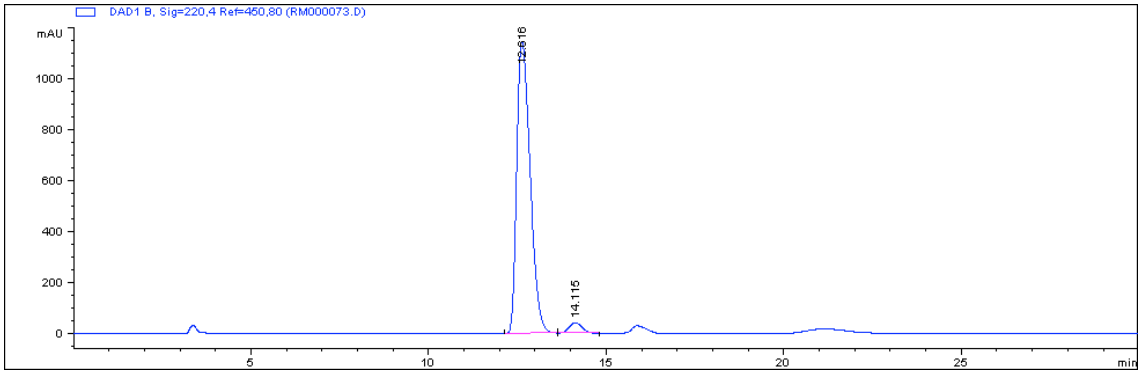
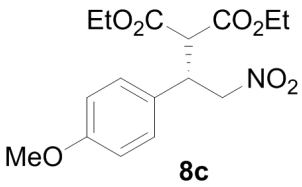


#	Time	Area	Height	Width	Area%	Symmetry
1	12.822	13392.6	538.4	0.3862	50.097	0.685
2	14.217	13340.4	496.3	0.4192	49.903	0.713



#	Time	Area	Height	Width	Area%	Symmetry
1	12.616	29971.2	1149.6	0.4034	96.381	0.592
2	14.115	1125.5	42.8	0.3996	3.619	0.901



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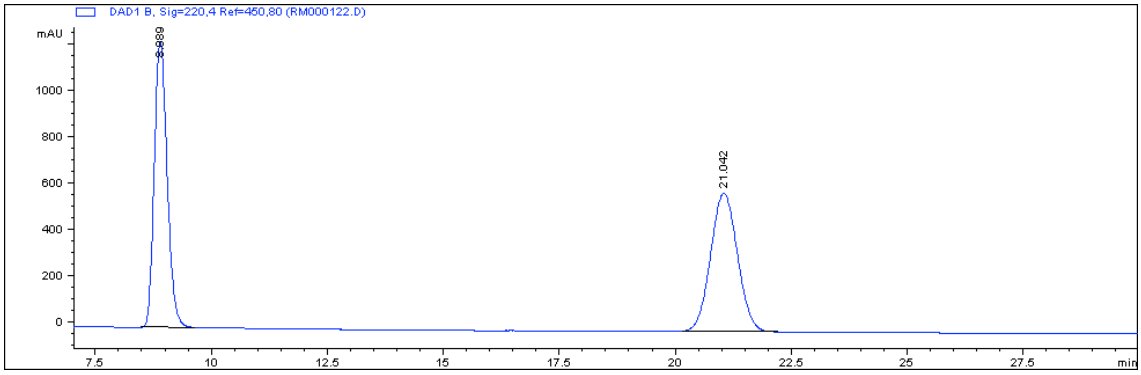
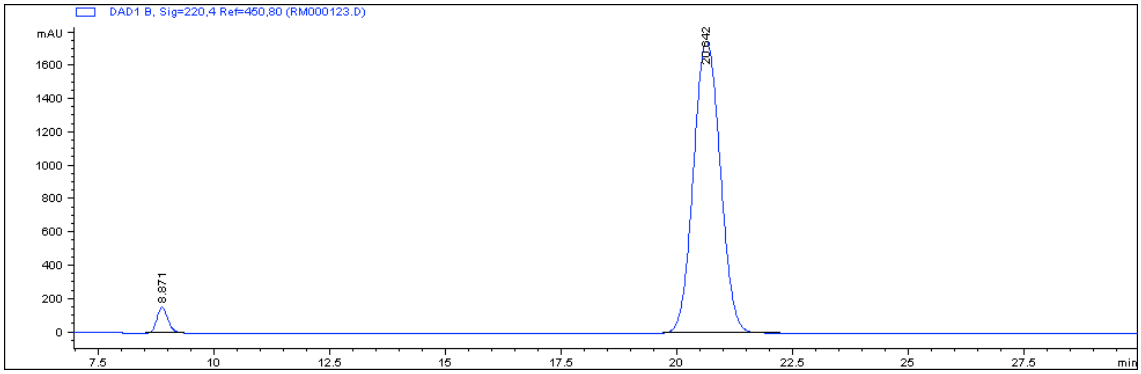
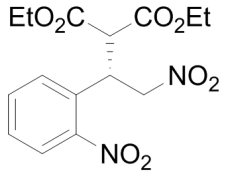


#	Time	Area	Height	Width	Area%	Symmetry
1	8.889	25492.3	1262.9	0.2995	51.375	0.817
2	21.042	24128.1	598.2	0.5057	48.625	0.988



#	Time	Area	Height	Width	Area%	Symmetry
1	8.871	2408.6	151.5	0.2649	3.241	0.843
2	20.642	71906.4	1761	0.6807	96.759	0.943



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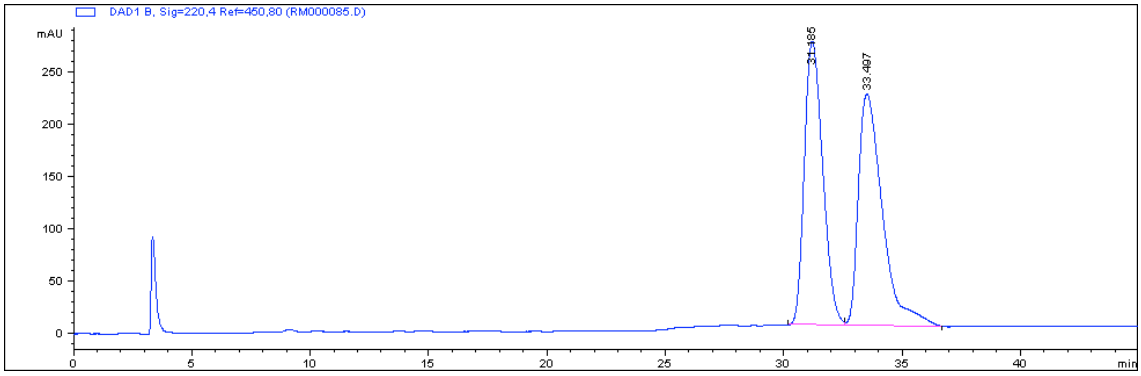
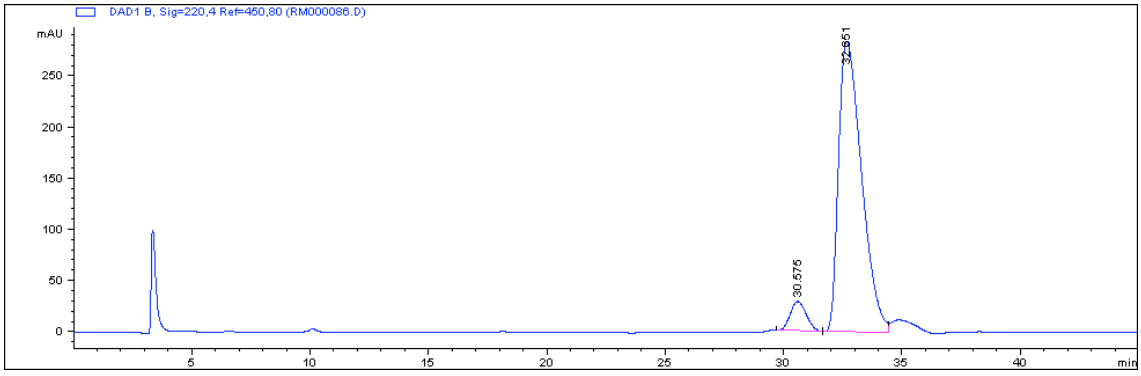
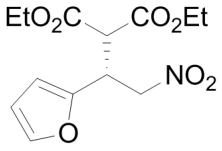


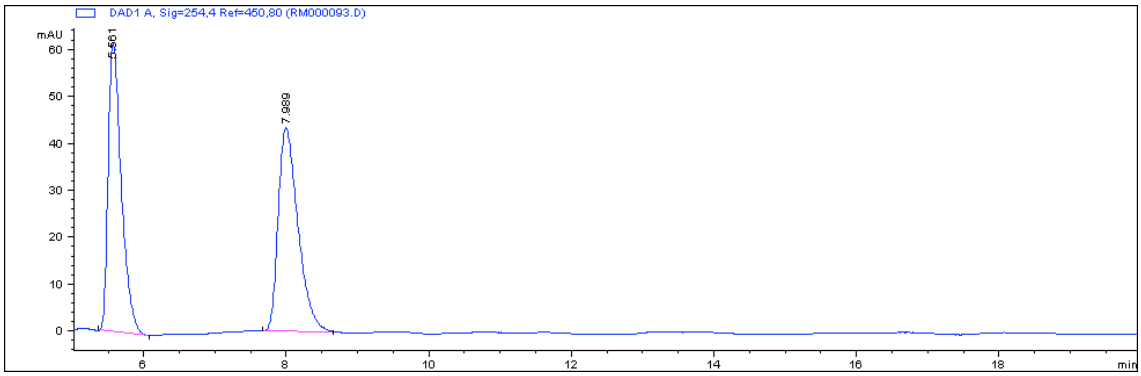
#	Time	Area	Height	Width	Area%	Symmetry
1	31.185	14764.5	272	0.8284	48.349	0.709
2	33.497	15773.1	222	1.0402	51.651	0.51



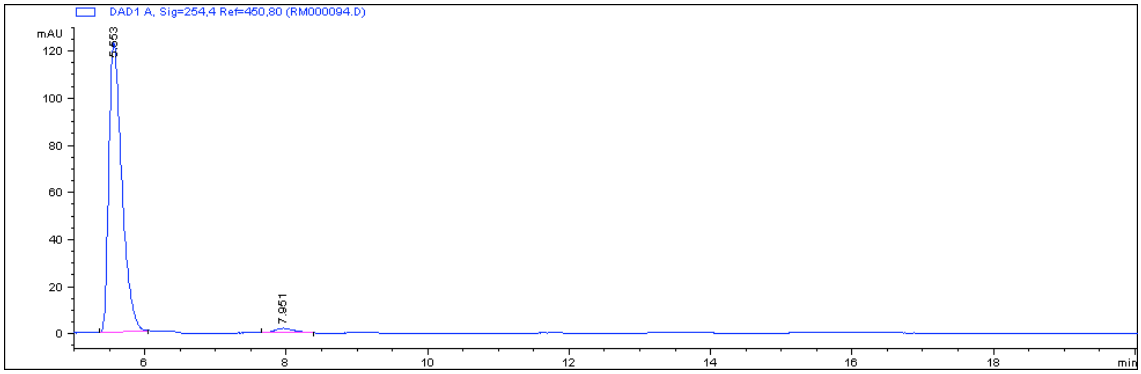
#	Time	Area	Height	Width	Area%	Symmetry
1	30.575	1367.5	28.9	0.6161	6.633	0.803
2	32.651	19249	284.1	1.0304	93.367	0.522



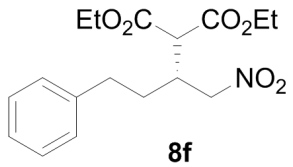
8e



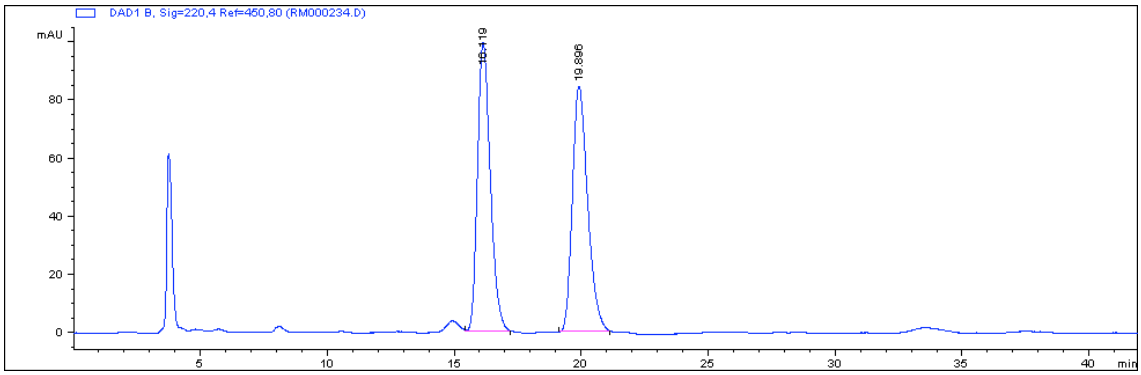
#	Time	Area	Height	Width	Area%	Symmetry
1	5.561	792.2	61.7	0.1946	48.689	0.546
2	7.989	834.9	43.3	0.2887	51.311	0.606



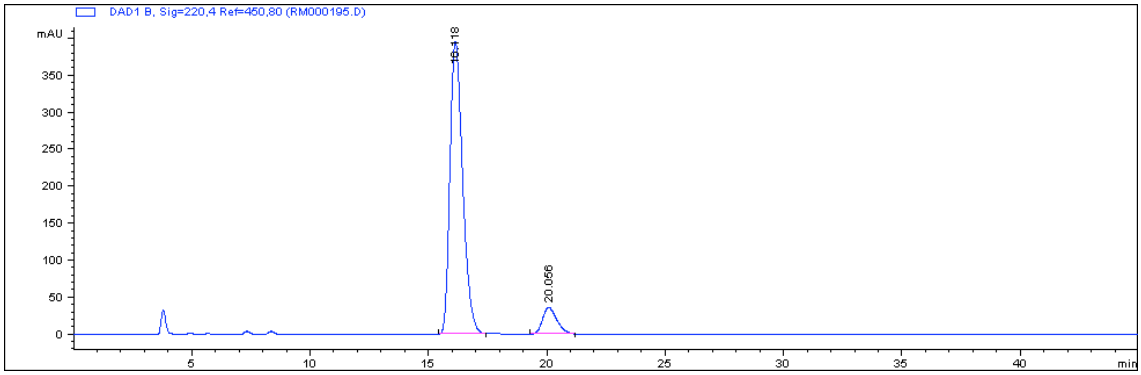
#	Time	Area	Height	Width	Area%	Symmetry
1	5.553	1565.2	123.5	0.1895	97.713	0.551
2	7.951	36.6	1.9	0.2555	2.287	0.675



8f



#	Time	Area	Height	Width	Area%	Symmetry
1	16.119	3513.9	99.7	0.5361	49.785	0.737
2	19.896	3544.3	84.5	0.6208	50.215	0.73



#	Time	Area	Height	Width	Area%	Symmetry
1	16.118	14740.6	395.7	0.5722	90.542	0.704
2	20.056	1539.9	36.2	0.624	9.458	0.699