Electronic Supporting Information for

Organocatalytic enantioselective conjugate addition of nitromethane to alkylidenemalonates: Asymmetric synthesis of pyrrolidine-3-carboxylic acid derivatives

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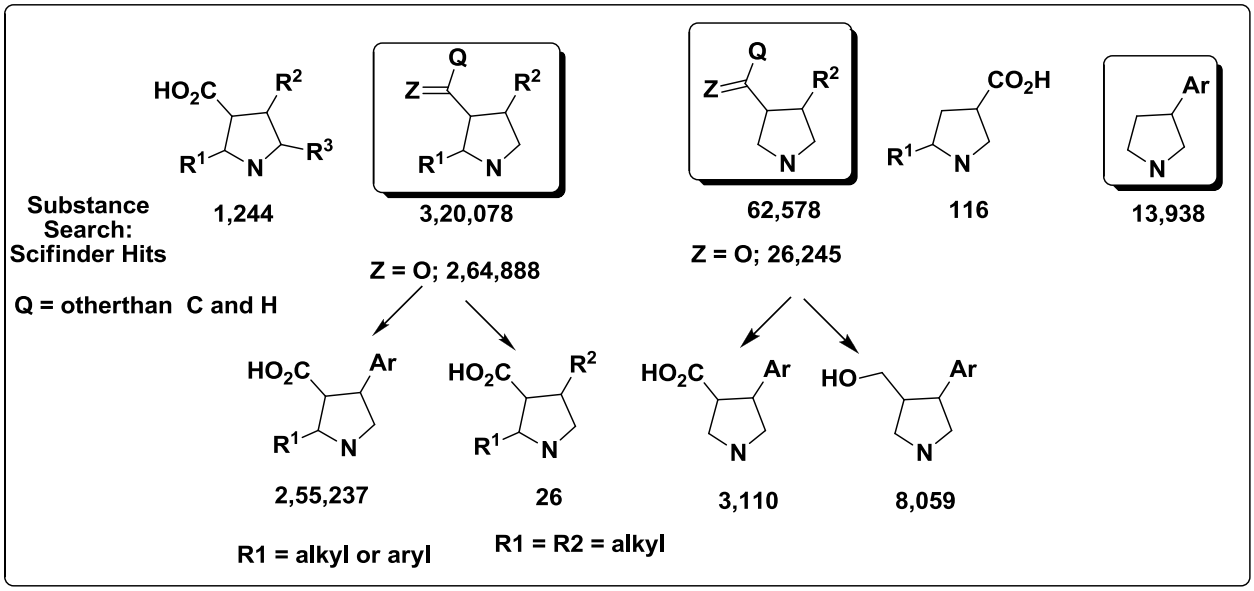
Contents

General information: All the reactions were carried out using oven dried glassware under an atmosphere of Argon (Ar). All reagents were used as purchased from commercial supplier without further purification. Solvents were dried and distilled following usual protocols. Flash column chromatography was performed in all cases using the indicated solvent system on Rankem silica gel (230-400 mesh) purchased from Rankem India. Analytical thin layer chromatography was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness) and compounds were visualized by irradiation of UV light. The ^{1}H NMR and ^{13}C NMR spectra were measured with Bruker-200 (200 MHz) and Bruker-400 (400 MHz) using $CDCl_3$. ^{1}H NMR chemical shifts are expressed in ppm (δ) relative to $CDCl_3$ (δ = 7.26) and ^{13}C NMR chemical shifts are expressed in ppm (δ) relative to $CDCl_3$ resonance (δ = 77.0). High performance liquid chromatography (HPLC) analyses were conducted using chiralpack AD-H column (0.46 cm x 15 cm). Specific optical rotation values were measured on Jasco-P1200 polarimeter.

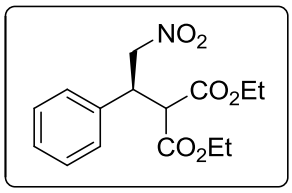
Catalysts **A-B**[1] and **C-F**[2] were prepared according to literature procedures and all the spectral data matches with the desire compounds.

Sci-Finder substructure search on March 2012

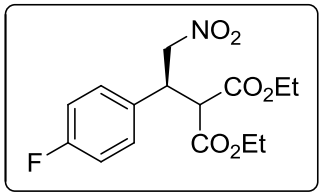


General procedure for the enantioselective addition of nitromethane to alkylidene malonate: Under argon atmosphere to a stirred solution of benzylidene malonate **5a** (0.10 g, 0.40 mmol) in nitromethane (1.1 mL, 50 equiv) was added organocatalyst **C** (0.023 g, 0.10 mmol) at room temperature (25 °C). The resulting mixture was stirred at the same temperature and monitored by TLC. After being stirred for 4 days reaction mixture was concentrated in vacuum under rt. The residue was purified by flash column chromatography on silica gel (Hexanes/EtOAc = 9/1) to afford the desired product **6a** (0.083 g, 67%).

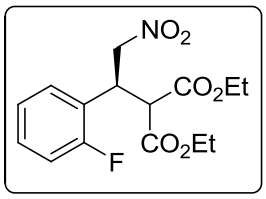
(*S*)-Diethyl-2-(2-nitro-1-phenylethyl) malonate (6a): The product was prepared by following the general procedure and was obtained as a colourless liquid in 67% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.29-7.24 (m, 5H), 4.91-4.86 (m, 2H), 4.29-4.17 (m, 3H), 4.00 (q, *J* = 7.0 Hz, 2H), 3.81 (d, *J* = 9.2 Hz, 1H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.04 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.6, 167.0, 136.4, 129.1 (2C), 128.5, 128.2 (2C), 77.8, 62.3, 62.0, 55.2, 43.1, 14.1, 13.9. **LC-MS** (ESI) m/z: 310.2 $[M+H]^+$, 327.2 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 85/15; flow rate 1.0 mL/min; λ = 254 nm; t_R = 7.6 min (minor), 21.7 min (major)] ee 72%. $[\alpha]^{25}_D$ = +6.12 (c, 1.30, $CHCl_3$). The absolute stereochemistry of the addition product was assigned as (*S*) by comparison of the optical data with literature reported value[3] $[\alpha]^{25}_D$ = +7.30 (c, 1.07, $CHCl_3$).



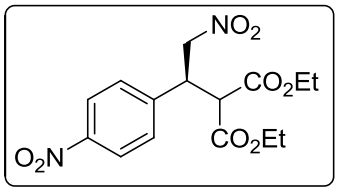
(*S*)-Diethyl-2-(1-(4-fluorophenyl)-2-nitroethyl) malonate (6b): The product was prepared by following the general procedure and was obtained as a colourless liquid in 70% yield. $[\alpha]^{25}_D$ = +7.17 (c, 1.11, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.26-7.19 (m, 2H), 7.01 (t, *J* = 8.4 Hz, 2H), 4.96-4.76 (m, 2H), 4.28-4.17 (m, 3H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.77 (d, *J* = 9.4 Hz, 1H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.5, 166.9, 162.7 (d, *J* = 246.5 Hz), 132.2, 130.0 (d, *J* = 8.0 Hz), 116.1 (d, *J* = 21.5 Hz), 77.8, 62.4, 62.2, 55.1, 42.5, 14.1, 13.9. **LC-MS** (ESI) m/z: 328.2 $[M+H]^+$, 345.3 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ = 254 nm; t_R = 5.5 min (minor), 18.9 min (major)] ee 98%.



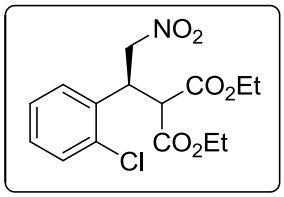
(*S*)-Diethyl-2-(1-(2-fluorophenyl)-2-nitroethyl) malonate (6c): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 68% yield. $[\alpha]^{25}_{D}$ = +3.84 (c, 1.41, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.29-7.21 (m, 2H), 7.08-7.02 (m, 2H), 4.94-4.45 (m, 2H), 4.45-4.39 (m, 1H), 4.26-4.18 (m, 2H), 4.00-3.93 (m, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.2, 166.6, 160.9 (d, *J* = 245 Hz), 130.6 (d, *J* = 4.0 Hz), 130.2 (d, *J* = 8.6 Hz), 124.4 (d, *J* = 3.3 Hz), 123.0 (d, *J* = 13.0 Hz), 115.9 (d, *J* = 21.8 Hz), 76.2 (d, *J* = 2.5 Hz), 62.1, 61.8, 53.2 (d, *J* = 2.1 Hz), 38.5, 13.8, 13.6. **LC-MS** (ESI) m/z: 328.2 $[M+H]^+$, 345.4 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ= 254 nm; t_R = 4.0 min (minor), 8.8 min (major)] ee 76%.



(*S*)-Diethyl-2-(2-nitro-1-(4-nitrophenyl) ethyl) malonate (6d): The product was prepared by following the general procedure and was obtained as a white solid in 76% yield. $[\alpha]^{25}_{D}$ = +4.83 (c, 0.78, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 5.02-4.83 (m, 3H), 4.35 (m, 1H), 4.23 (q, *J* = 7.0 Hz 2H), 4.04 (q, *J* = 7.0 Hz, 2H), 3.82 (d, *J* = 9.0 Hz, 1H), 1.26 (t, *J* = 7.0 Hz, 3H), 1.09 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.1, 166.6, 148.0, 144.0, 129.5 (2C), 124.3 (2C), 77.1, 62.7, 62.5, 54.6, 42.8, 14.2, 14.0. **LC-MS** (ESI) m/z: 355.3 $[M+H]^+$, 372.3 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ= 254 nm; t_R = 5.3 min (minor), 9.8 min (major)] ee 97%.

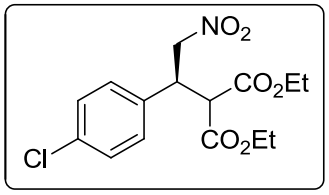


(*S*)-Diethyl-2-(1-(2-chlorophenyl)-2-nitroethyl) malonate (6e): The product was prepared by following the general procedure and was obtained as a colourless liquid in 69% yield. $[\alpha]^{25}_{D}$ = +8.42 (c, 1.18, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.44-7.40 (m, 1H), 7.28-7.21 (m, 3H),5.11 (dd, *J*= 13.5 Hz, 8.6 Hz, 1H), 4.91 (dd, *J* = 13.5 Hz, 4.4 Hz, 1H), 4.75 (dt, *J* = 8.6 Hz, 4.4 Hz, 1H), 4.25 (q, *J* = 7.0 Hz, 2H), 4.20-4.13 (m, 3H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.15 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.6, 167.0, 134.3, 134.0, 130.6, 129.7, 129.1, 127.4, 75.9, 62.3, 62.2, 53.3, 39.6, 14.1, 13.9. **LC-MS** (ESI) m/z: 344.2 $[M+H]^+$, 361.2 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column

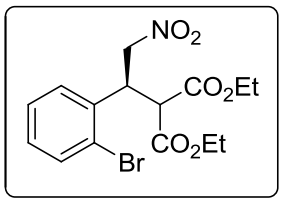


[Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ= 254 nm; t_R = 3.9 min (minor), 17.6 min (major)] ee 76%.

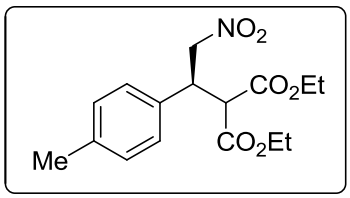
(*S*)-Diethyl-2-(1-(4-chlorophenyl)-2-nitroethyl) malonate (6f): The product was prepared by following the general procedure and was obtained as a gummy liquid in 67% yield. $[\alpha]^{25}_D$ = +6.57 (c, 1.12, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.29 (d, *J* = 8.6 Hz, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 4.89-4.82 (m, 2H), 4.26-4.16 (m, 3H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.76 (d, *J* = 9.2 Hz, 1H), 1.25 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.3, 166.7, 134.8, 134.4, 129.5 (2C), 129.2 (2C), 77.4, 62.3, 62.1, 54.8, 42.4, 14.0, 13.8. **LC-MS** (ESI) m/z: 344.2 $[M+H]^+$, 361.3 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ= 254 nm; t_R = 6.7 min (minor), 17.6 min (major)] ee 80%.



(*S*)-Diethyl-2-(1-(2-bromophenyl)-2-nitroethyl) malonate (6g): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 64% yield. $[\alpha]^{25}_D$ = +4.09 (c, 1.10, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.24 (m, 2H), 7.19-7.10 (m, 1H), 5.16-5.05 (m, 1H), 4.98-4.87 (m, 1H), 4.80-4.71 (m, 1H), 4.25-4.03 (m, 5H), 1.22 (t, *J* = 7.0 Hz, 3H), 1.11 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.4, 166.8, 135.4, 133.8, 129.7, 128.6, 127.9, 124.9, 75.8, 62.1 (2C), 53.3, 41.5, 14.0, 13.8. **LC-MS** (ESI): m/z 390.0 $[M+H]^+$, 407.0 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ = 254 nm; t_R = 3.6 min (minor), 16.5 min (major)] ee 70%.

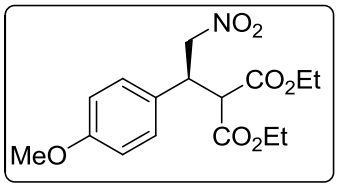


(*S*)-Diethyl-2-(2-nitro-1-(p-tolyl) ethyl) malonate (6h): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 65% yield. $[\alpha]^{25}_D$ = +3.72 (c, 1.17, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.09 (s, 4H), 4.94-4.71 (m, 2H), 4.25-4.11 (m, 3H), 3.95 (q, *J* = 7.2 Hz, 2H), 3.77 (d, *J* = 9.4 Hz, 1H), 2.28 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.04 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.4, 166.8, 138.0, 133.0, 129.5 (2C), 127.8 (2C), 77.7, 62.0, 61.8, 55.0, 42.6, 21.0, 13.9, 13.7. **LC-MS** (ESI): m/z 324.3 $[M+H]^+$, 341.1 $[M+NH_4]^+$. The enantiomeric excess was determined by

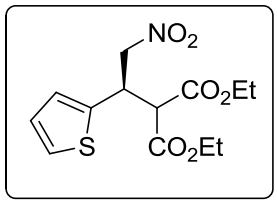


HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ= 254 nm; t_R = 4.8 min (minor), 11.8 min (major)] ee 68%.

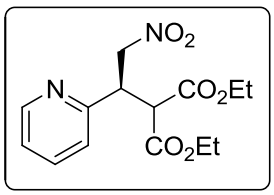
(*S*)-Diethyl-2-(1-(4-methoxyphenyl)-2-nitroethyl) malonate (6i): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 64% yield. $[\alpha]^{25}_D$ = +4.21 (c, 1.43, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.95-4.78 (m, 2H), 4.32-4.18 (m, 3H), 4.05 (q, *J* = 7.2 Hz, 2H), 3.82 (d, *J* = 9.0 Hz, 1H), 3.81 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.11 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.5, 166.8, 159.3, 129.1 (2C), 127.9, 114.2 (2C), 77.8, 62.0, 61.7, 55.1, 42.2, 13.9, 13.7. **LC-MS** (ESI): m/z 340.3 $[M+H]^+$, 357.1 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ = 254 nm; t_R = 5.7 min (minor), 14.4 min (major)] ee 59%.



(*R*)-Diethyl-2-(2-nitro-1-(thiophen-2-yl) ethyl) malonate (6j): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 62% yield. $[\alpha]^{25}_D$ = -3.14 (c, 0.65, $CHCl_3$) **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.32-7.20 (m, 1H), 7.00-6.89 (m, 2H), 5.03-4.86 (m, 2H), 4.55 (m, 1H), 4.23 (q, *J* = 7.0 Hz, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.86 (d, *J* = 8.0 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.4, 167.0, 138.7, 127.2, 127.0, 125.7, 78.3, 62.4, 62.3, 55.7, 38.6, 14.1, 14.0. **LC-MS** (ESI) m/z: 316.2 $[M+H]^+$, 333.2 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ= 254 nm; t_R = 4.8 min (minor), 8.7 min (major)] ee 66%.

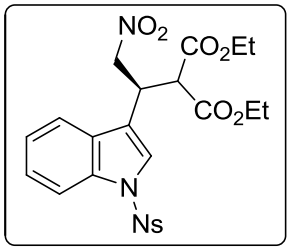


(*R*)-Diethyl-2-(2-nitro-1-(pyridin-2-yl) ethyl) malonate (6k): The product was prepared by following the general procedure and was obtained as a dark red coloured liquid in 58% yield. $[\alpha]^{25}_D$ = -1.14 (c, 0.62, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 8.51 (d, *J* = 4.2 Hz, 1H), 7.62 (dt, *J* = 7.6 Hz, 1.5 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 1H), 7.17 (dd, *J* = 7.6 Hz, 5.0 Hz, 1H), 5.10 (dd, *J* = 13.6 Hz, 9.8 Hz, 1H), 4.80 (dd, *J* = 13.6 Hz, 4.0 Hz, 1H), 4.35 (dt, *J* = 9.4 Hz, 4.0 Hz, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.96 (d, *J* = 9.2 Hz, 1H), 1.26 (t, *J* = 7.0 Hz, 3H),



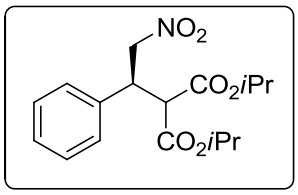
1.08 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.7, 167.2, 156.7, 149.7, 136.9, 124.7, 123.0, 76.7, 62.3, 62.0, 54.2, 44.0, 14.1, 14.0. **LC-MS** (ESI) m/z: 311.2 $[M+H]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ= 254 nm; t_R = 9.2 min (minor), 10.7 min (major)] ee 63%.

(*S*)-diethyl-2-(2-nitro-1-(1-((4-nitrophenyl) sulfonyl)-1H-indol-3-yl) ethyl)malonate (6l): The



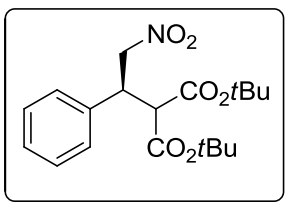
product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 57% yield. $[\alpha]^{25}_D$ = -20.15 (c, 0.75, $CHCl_3$) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.25 (d, *J* = 8.8 Hz, 2H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.93 (m, 1H), 7.55 (m, 2H), 7.39-7.29 (m, 2H), 5.00 (dd, *J* = 8.2 Hz, 12.8 Hz, 1H), 4.90 (dd, *J* = 4.8 Hz, 12.8 Hz, 1H), 4.46 (dt, *J* = 8.0 Hz, 4.8 Hz, 1H), 4.24-4.14 (m, 2H), 4.06-3.97 (m, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 167.0, 166.7, 150.6, 142.5, 134.7, 129.3, 128.0 (2C), 126.0, 124.7, 124.5, 124.4 (2C), 119.4, 119.3, 113.7, 76.6, 62.2, 62.1, 53.4, 34.0, 13.8, 13.6. **LC-MS** (ESI) m/z: 532.0 $[M+H]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ= 254 nm; t_R = 12.7 min (major), 16.4 min (minor)] ee 55%.

(*S*)-Diisopropyl-2-(2-nitro-1-phenylethyl) malonate (6-isopropyl): The product was prepared



by following the general procedure and was obtained as a colourless liquid in 47% yield. $[\alpha]^{25}_D$ = +7.27 (c, 1.15, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.40-7.21 (m, 5H), 5.08 (m, 1H), 4.99-4.76 (m, 3H), 4.25-4.14 (m, 1H), 3.74 (d, *J* = 9.6 Hz, 1H), 1.24 (d, *J* = 6.2 Hz, 6H), 1.06 (d, *J* = 6.2 Hz, 3H), 1.01 (d, *J* = 6.2 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.0, 166.2, 136.2, 128.8 (2C), 128.2, 128.0 (2C), 77.8, 69.8, 69.5, 55.1, 42.8, 21.5, 21.4, 21.22, 21.20. **LC-MS** (ESI) m/z: 338.0 $[M+H]^+$, 355.2 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ= 254 nm; t_R = 4.0 min (major), 7.4 min (minor)] ee 73%.

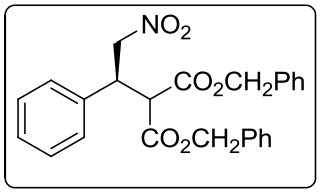
(*S*)-Di-tert-butyl-2-(2-nitro-1-phenylethyl) malonate (6-tert-butyl): The product was prepared



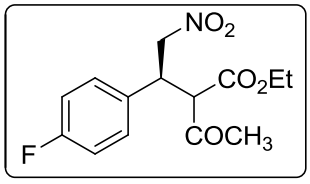
by following the general procedure and was obtained as a white solid in

27% yield. $[\alpha]^{25}_D$ = +6.74 (c, 1.05, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.27 (m, 5H), 4.93 (dd, *J* = 12.7, 4.6 Hz, 1H), 4.79 (dd, *J* = 12.7, 9.5 Hz, 1H), 4.12 (dt, *J* = 9.6 Hz, 4.6 Hz, 1H), 3.61 (d, *J* = 9.8 Hz, 1H), 1.46 (s, 9H), 1.22 (s, 9H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.1, 166.2, 136.8, 129.0 (2C), 128.5 (2C), 128.3, 83.1, 82.5, 78.4, 56.7, 43.3, 28.0 (3C), 27.7 (3C). **LC-MS** (ESI) m/z: 366.2 $[M+H]^+$, 383.3 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ= 254 nm; t_R = 3.6 min (major), 7.3 min (minor)] ee 51%.

(*S*)-Dibenzyl-2-(2-nitro-1-phenylethyl) malonate (6-dibenzyl): The product was prepared by following the general procedure and was obtained as a white solid in 67% yield. $[\alpha]^{25}_D$ = +2.73 (c, 1.01, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.35-7.06 (m, 15H), 5.16 (s, 2H), 4.94 (s, 2H), 4.84 (d, *J*= 6.8 Hz, 2H), 4.26 (m, 1H), 3.93 (d, *J*= 9.2 Hz, 1H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 167.4, 166.7, 136.2 (2C), 134.9 (2C), 129.2 (2C), 128.9 (2C), 128.8 (2C), 128.7 (2C), 128.6 (2C), 128.5 (2C), 128.2 (2C), 77.6, 68.0, 67.9, 55.2, 43.2. **LC-MS** (ESI) m/z: 451.2 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 75/25; flow rate 1.0 mL/min; λ= 254 nm; t_R = 6.5 min (minor), 18.4 min (major)] ee 78%.

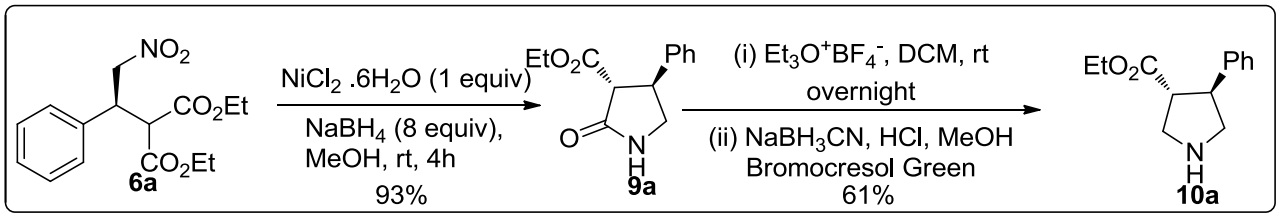


(3*S*)-Ethyl-2-acetyl-3-(4-fluorophenyl)-4-nitrobutanoate (8): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 78% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ major diastereomer 7.21 (dd, *J* = 8.0, 5.2 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 4.82-4.77 (m, 2H), 4.23 (q, *J* = 8.2 Hz, 2H), 4.05 (d, *J* = 10.8 Hz, 1H), 4.17-4.03 (m, 1H), 2.29 (s, 3H), 1.27 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 200.8, 167.0, 162.4 (d, *J* = 246.3 Hz), 132.1, 129.6 (d, *J* = 8.3 Hz, 2C), 116.0 (d, *J* = 21.8 Hz, 2C), 77.8, 61.9, 41.5, 29.6, 25.2, 13.7. **LC-MS** (ESI) m/z: 298.2 $[M+H]^+$, 315.2 $[M+NH_4]^+$. The enantiomeric excess was determined by HPLC analysis using Chiralpak AD-H column [Hexane/*i*-PrOH 85/15; flow rate 1.0 mL/min; λ= 254 nm; t_R = 3.3 min (major), 6.4 min (minor)] ee 70%.

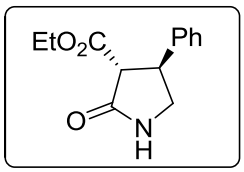


General procedure for the synthesis of compounds 9a and 10a:

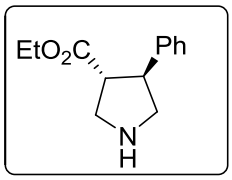
The compound (3*R*, 4*S*)-Ethyl 4-phenylpyrrolidine-3-carboxylate (**10a**) was synthesized following literature procedure.[4]



(3*R*, 4S)-Ethyl-2-oxo-4-phenylpyrrolidine-3-carboxylate (9a): The product was obtained as a brown solid in 93% yield. $[\alpha]^{25}_{D}$ = +66.43 (c, 0.9, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.36-7.24 (m, 5H), 6.62 (br s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.09 (q, *J*= 8.4 Hz, 17.4 Hz, 1H), 3.87-3.78 (m, 1H), 3.55 (d, *J* = 9.4 Hz, 1H), 3.43 (t, *J*= 8.8 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 172.6, 169.1, 139.8, 128.9, 127.5, 126.9, 61.8, 55.1, 47.6, 44.3, 14.0. **HRMS** (ESI) calculated for $C_{13}H_{16}NO_3$, 234.1130 m/z $[M+H]^+$ found 234.1131.



(3*R*, 4S)-Ethyl-4-phenylpyrrolidine-3-carboxylate (10a): The product was obtained as a yellow gummy liquid in 61% yield. $[\alpha]^{25}_{D}$ = +33.46 (c, 0.65, $CHCl_3$). **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.36-7.23 (m, 5H), 4.13 (q, *J*= 7.0 Hz, 2H), 3.58-3.45 (m, 2H), 3.39-3.34 (m, 2H), 3.12-2.87 (m, 4H), 2.47 (s, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (50 MHz, $CDCl_3$): δ 174.5, 141.7, 128.2 (2C), 126.8 (2C), 126.3, 60.3, 55.8, 52.4, 51.7, 50.1, 13.7. **HRMS** (ESI) calculated for $C_{13}H_{18}NO_2$, 220.1138 m/z $[M+H]^+$ found 220.1353.

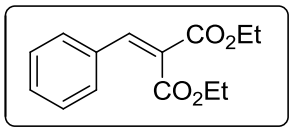


General procedure for substrate preparation:

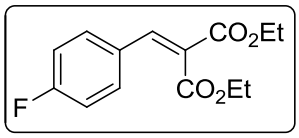
All the substrates **5a-l** and **7** were prepared according to literature[5] reported procedure.

In a round bottomed flask equipped with a Dean-Stark apparatus diethyl malonate (1.51 g, 9.43 mmol) and benzaldehyde (1.0 g, 9.43 mmol) was taken in anhydrous benzene (50 ml). Then

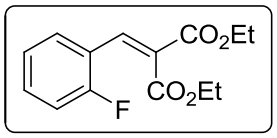
piperidine (cat. amount) and glacial acetic acid (cat. amount) were added to the mixture. The mixture was refluxed until the substrate disappeared. After the completion of the reaction the mixture was cooled, diluted with diethyl ether (50 ml) and water (25 ml). The organic layer was separated and washed successively with water (25 ml), HCl (1M) solution and sodium bicarbonate solution. The organic layer was dried and concentrated *in vacuo*. The crude product was purified by flash chromatography (hexane/EtOAc = 9/1) to afford the desired product (1.95 g, 83%).



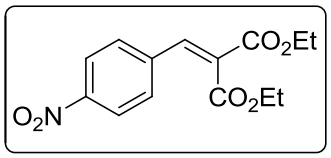
Diethyl-2-benzylidenemalonate (5a): The product was prepared by following the general procedure and was obtained as a yellow liquid in 83% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.72(s, 1H), 7.43-7.35 (m, 5H), 4.91-4.86 (m, 2H), 4.37-4.23 (m, 3H), 1.35-1.23 (m, 6H).



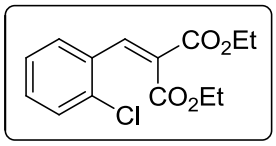
Diethyl-2-(4-fluorobenzylidene) malonate (5b): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 84% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.62 (s, 1H), 7.43-7.36(m,2H), 7.04-6.95 (m, 2H), 7.01 (t, *J*=8.4 Hz, 2H), 4.43-4.18 (m, 4H), 1.30-1.19 (m, 6H).



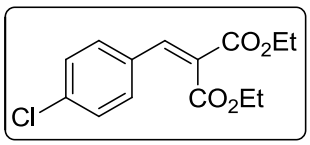
Diethyl-2-(2-fluorobenzylidene) malonate (5c): The product was prepared by following the general procedure and was obtained as gummy liquid in 79% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.90 (s, 1H), 7.48-7.32 (m, 2H), 7.15-7.04 (m, 2H), 4.30 (dq, *J*= 7.2 Hz, 14.2 Hz, 2.2 Hz, 4H), 1.33 (t, *J*= 7.2 Hz, 3H), 1.25 (t, *J*= 7.2 Hz, 3H).



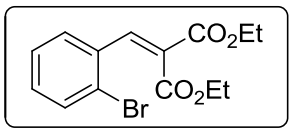
Diethyl-2-(4-nitrobenzylidene) malonate (5d): The product was prepared by following the general procedure and was obtained as pale yellow solid in 93% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 8.16 (d, *J*= 8.4 Hz, 2H), 7.68 (s, 1H), 7.53 (d, *J*= 8.4 Hz, 2H), 4.26 (q, *J*= 7.2 Hz, 14.2 Hz, 4H), 1.31-1.17 (m, 6H).



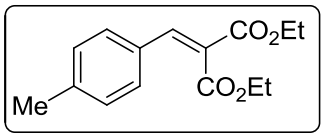
Diethyl-2-(2-chlorobenzylidene) malonate (5e): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 86% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.98(s, 1H), 7.42-7.35 (m, 2H), 7.31-7.15 (m, 2H), 4.32-4.14 (m, 4H), 1.29 (t, *J*= 7.0 Hz, 3H), 1.14 (t, *J*= 7.2 Hz, 3H).



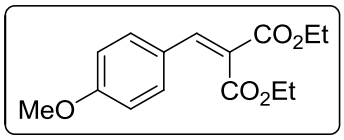
Diethyl-2-(4-chlorobenzylidene) malonate (5f): The product was prepared by following the general procedure and was obtained as a yellow liquid in 83% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.46-7.36 (m, 4H), 4.43-4.23 (m, 4H), 1.41-1.30 (m, 6H).



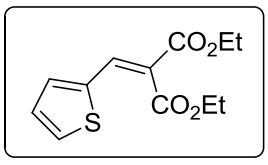
Diethyl-2-(2-bromobenzylidene) malonate (5g): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 78% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.66 (dd, *J*= 1.6 Hz, 7.4 Hz, 1H), 7.49-7.44 (m, 1H), 7.36-7.24 (m, 2H), 4.42-4.21 (m, 4H), 1.39 (t, *J*= 7.1 Hz, 3H), 1.21 (t, *J*= 7.1 Hz, 3H).



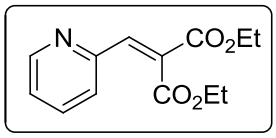
Diethyl-2-(4-methylbenzylidene) malonate (5h): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 84% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.63(s, 1H), 7.28(d, *J*=8.2Hz, 2H), 7.11 (d, *J*=8.0Hz, 2H), 4.29-4.17 (m, 4H), 2.3 (s, 3H), 1.29-1.20 (m, 6H).



Diethyl-2-(4-methoxybenzylidene) malonate (5i): The product was prepared by following the general procedure and was obtained as a brown gummy liquid in 78% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.71 (s, 1H), 7.46 (d, *J*= 8.8 Hz, 2H), 6.92 (d, *J*= 9.0 Hz, 2H), 4.45-4.27 (m, 4H), 3.87 (s, 8H), 1.40-1.33 (m, 6H).

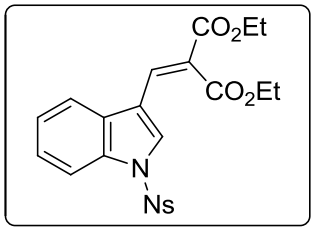


Diethyl-2-(thiophen-2-ylmethylene) malonate (5j): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 79% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.84(s, 1H), 7.52 (d, *J*= 5.0Hz, 1H), 7.37 (d, *J*=3.8Hz, 1H), 7.07 (dd, *J*=3.8 Hz, 5.0 Hz, 1H), 4.45-4.19 (m, 4H), 1.41-1.24 (m, 6H).

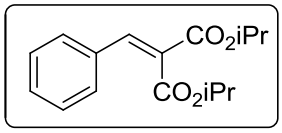


Diethyl-2-(pyridin-2-ylmethylene) malonate (5k): The product was prepared by following the general procedure and was obtained as yellow solid in 74% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 8.58 (d, *J*= 4.6 Hz, 1H), 7.70 (dt, *J*= 7.8 Hz, 1.8 Hz, 1H), 7.63 (s, 1H), 7.38 (d, *J*= 7.8 Hz, 1H), 7.27-7.21(m, 1H) , 4.45-4.26(m, 4H), 1.38-1.30 (m, 6H)

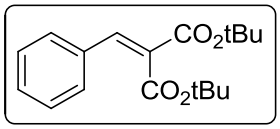
Diethyl-2-((1-((4-nitrophenyl) sulfonyl)-1H-indol-3-yl)methylene)malonate (5l): The product



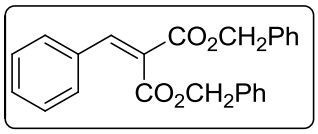
was prepared by following the general procedure and was obtained as yellow solid in 77% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 8.30 (d, *J*= 8.8 Hz, 2H), 8.07 (d, *J*= 9.0 Hz, 2H), 8.01-7.97 (m, 2H), 7.84 (s, 1H), 7.68 (dd, *J*= 1.8 Hz, 6.6 Hz, 1H), 7.47-7.33 (m, 2H), 4.47-4.28 (m, 4H), 1.41-1.32 (m, 6H).



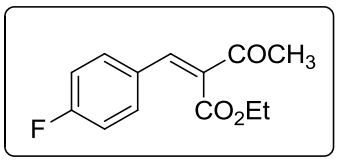
Diisopropyl-2-benzylidenemalonate (5-isopropyl): The product was prepared by following the general procedure and was obtained as a colorless liquid in 75% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.47-7.42 (m, 2H), 7.36-7.32 (m, 3H), 5.26-5.12 (m, 2H), 1.24-1.21 (m, 12H).



Di-tert-butyl-2-benzylidenemalonate (5-tertbutyl): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 81% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.55(s, 1H), 7.52-7.48(m, 2H), 7.39-7.34 (m, 3H), 1.53 (s, 9H), 1.52 (s, 9H).



Dibenzyl-2-benzylidenemalonate (5-dibenzyl): The product was prepared by following the general procedure and was obtained as white solid in 85% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.78(s, 1H), 7.35-7.22 (m, 15H), 5.06 (s, 2H), 4.84 (s, 4H).



(Z)-Ethyl-2-(4-fluorobenzylidene)-3-oxobutanoate (7): The product was prepared by following the general procedure and was obtained as a yellow gummy liquid in 83% yield. **^{1}H NMR** (200 MHz, $CDCl_3$): δ 7.42- 7.32 (m, 3H), 7.02-6.94 (m, 2H), 4.23 (q, *J* = 7.2 Hz, 14.4 Hz, 2H), 2.3 (s, 3H), 1.18 (t, *J* =7.0 Hz, 3H).

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2. B. Vakulya, S. Varga, A. Csampai, T. Soos, *Org. Lett*, **2005**, *7*, 1967.
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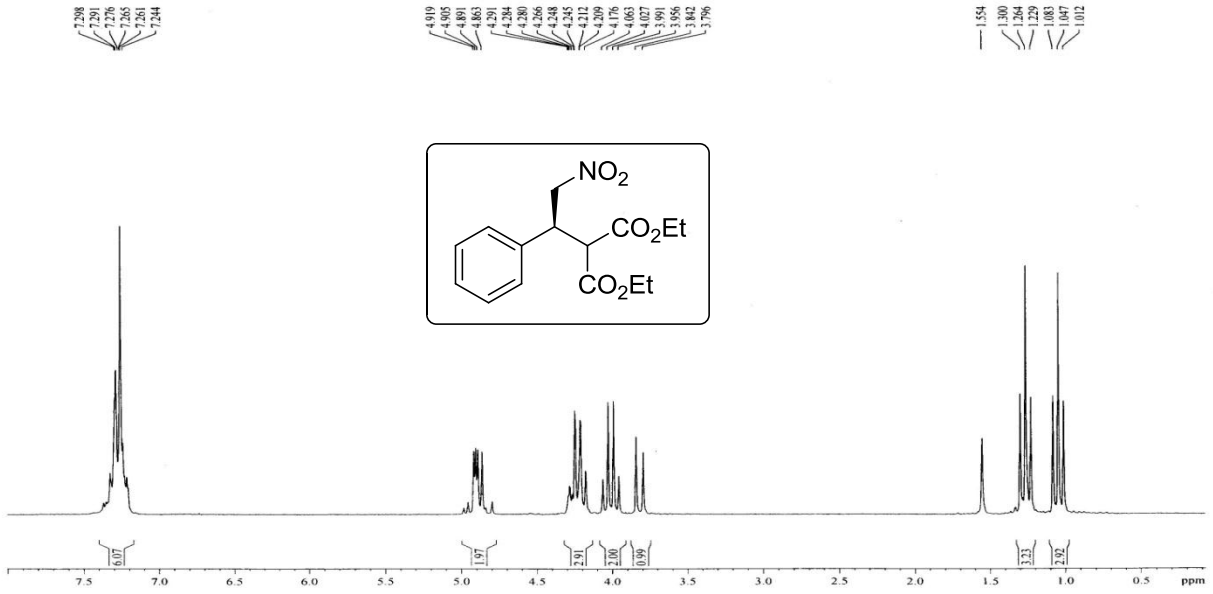
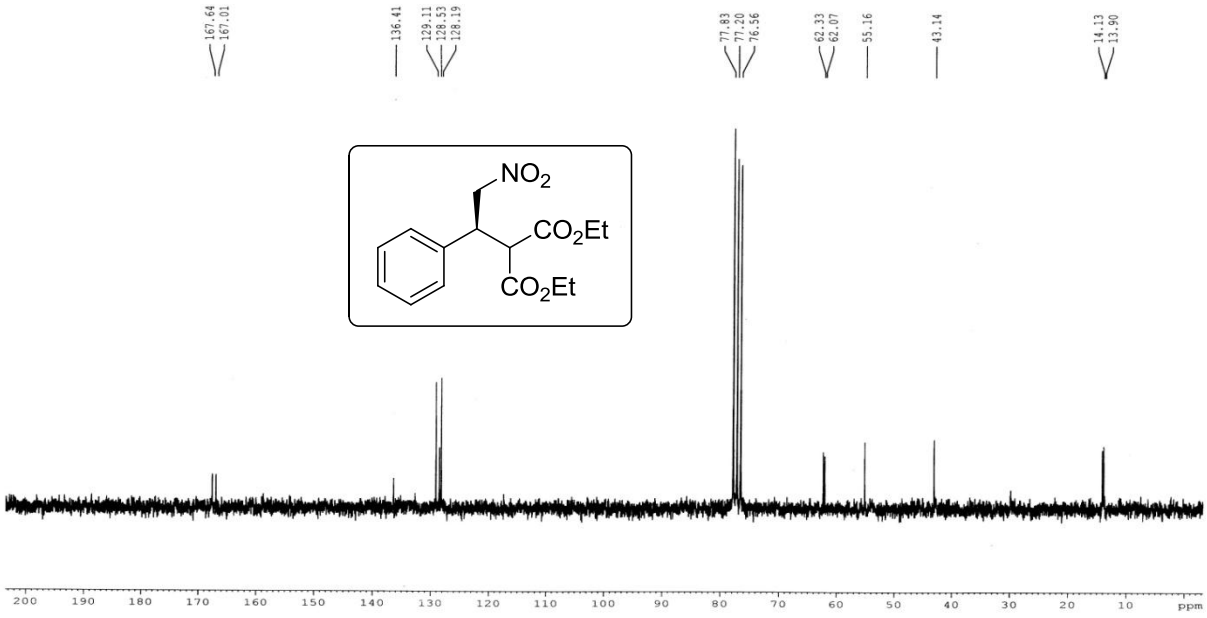
4. D. A. Evans, S. Mito, D. Seidel; *J. Am. Chem. Soc*. **2007**, *129*, 11583.
5. T. Wang, J. Liu, H. Zhong, H. Chen, Z. Lv, Y. Zhang, M. Zhang, D. Geng, C. Niu, Y. Li, K. Li; *Bioorg. Med. Chem. Lett*, **2011**, *21*, 3381

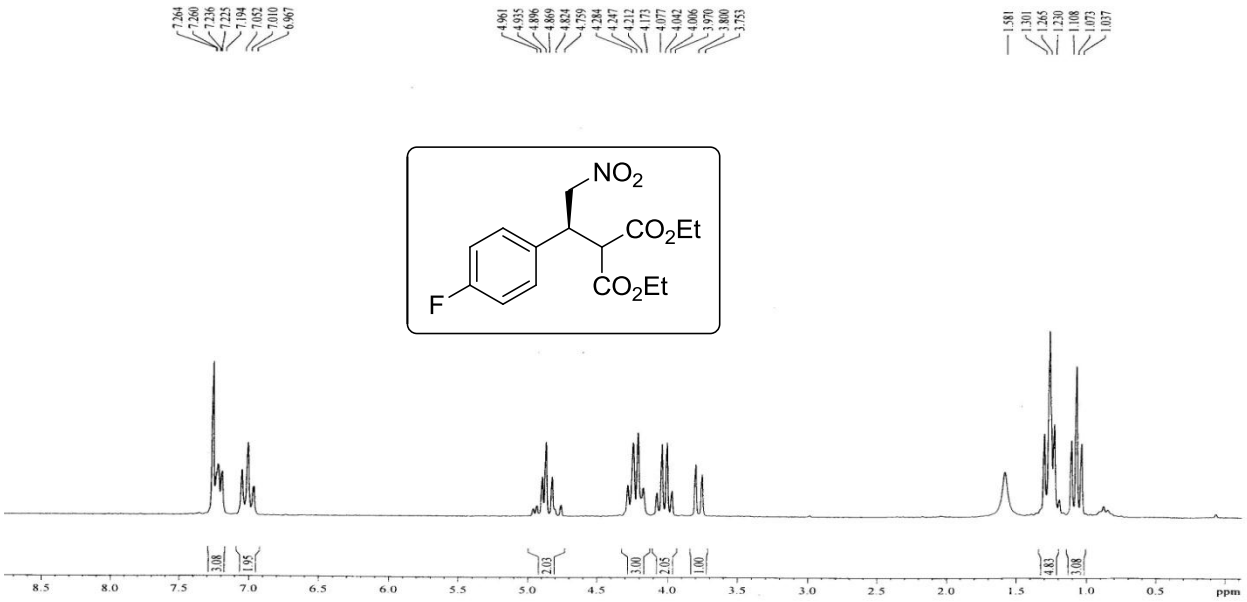
^{1}H- and ^{13}C NMR Spectra



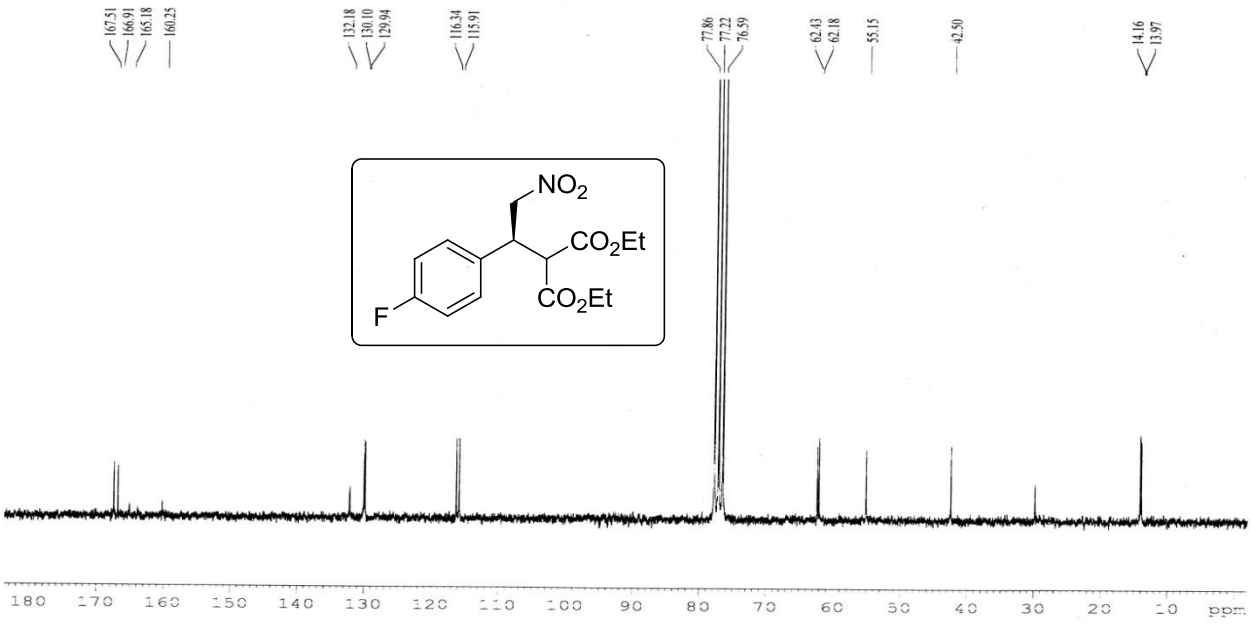
^{1}H NMR Spectrum of compound **6a** (200 MHz, $CDCl_3$)



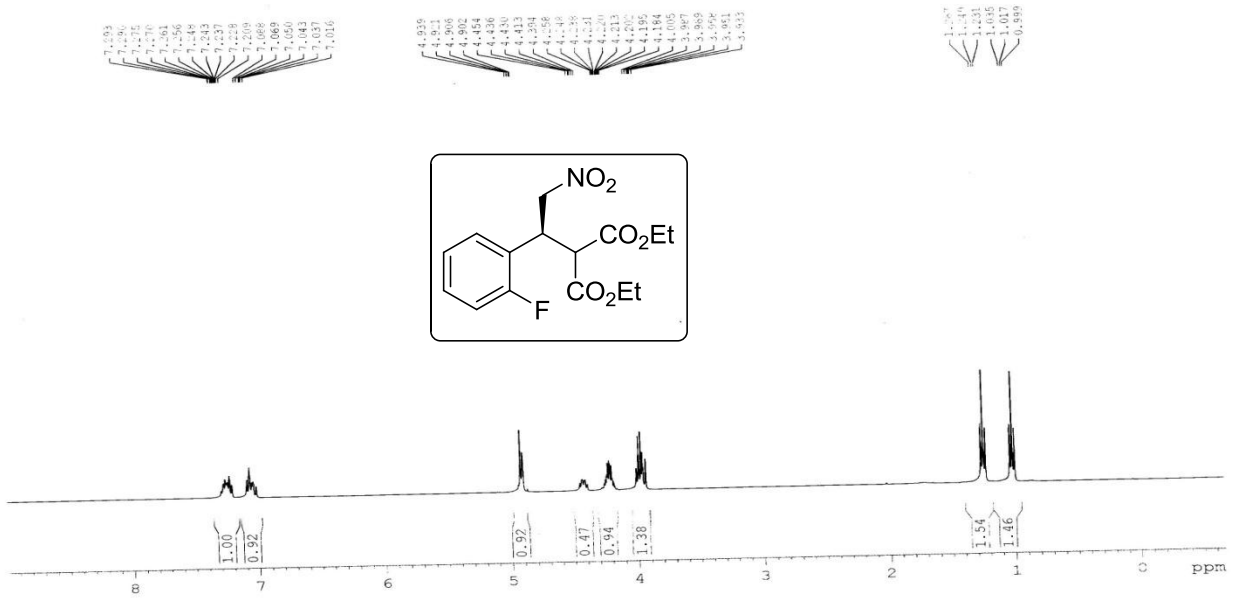
^{13}C NMR Spectrum of compound **6a** (50 MHz, $CDCl_3$).



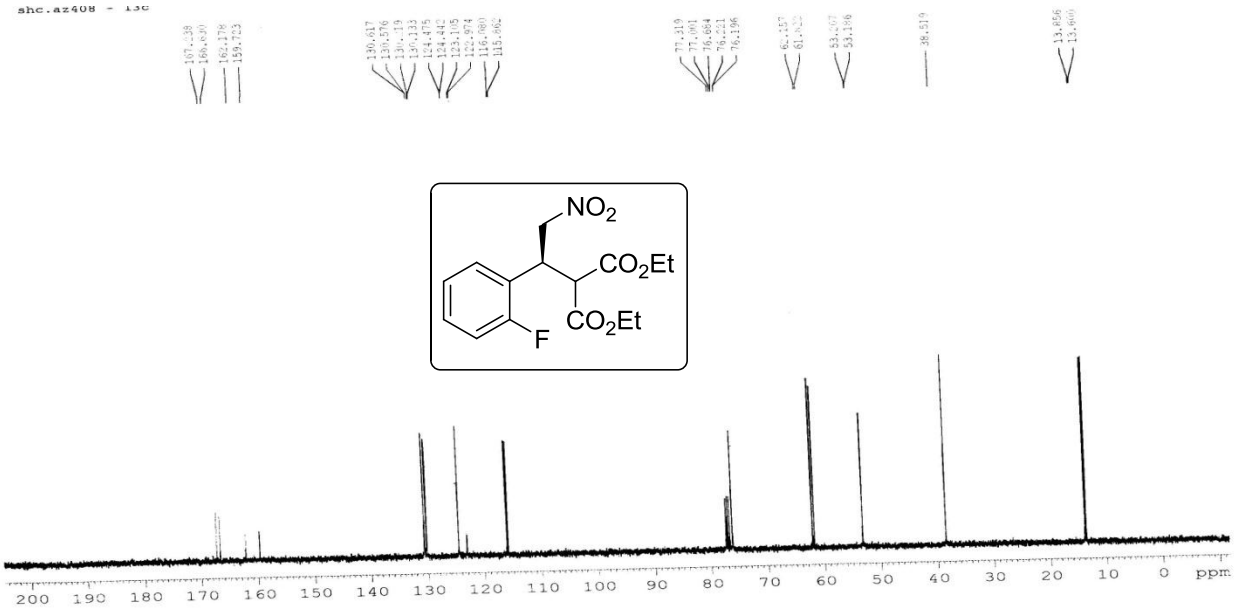
^{1}H NMR Spectrum of compound **6b** (200 MHz, $CDCl_3$)



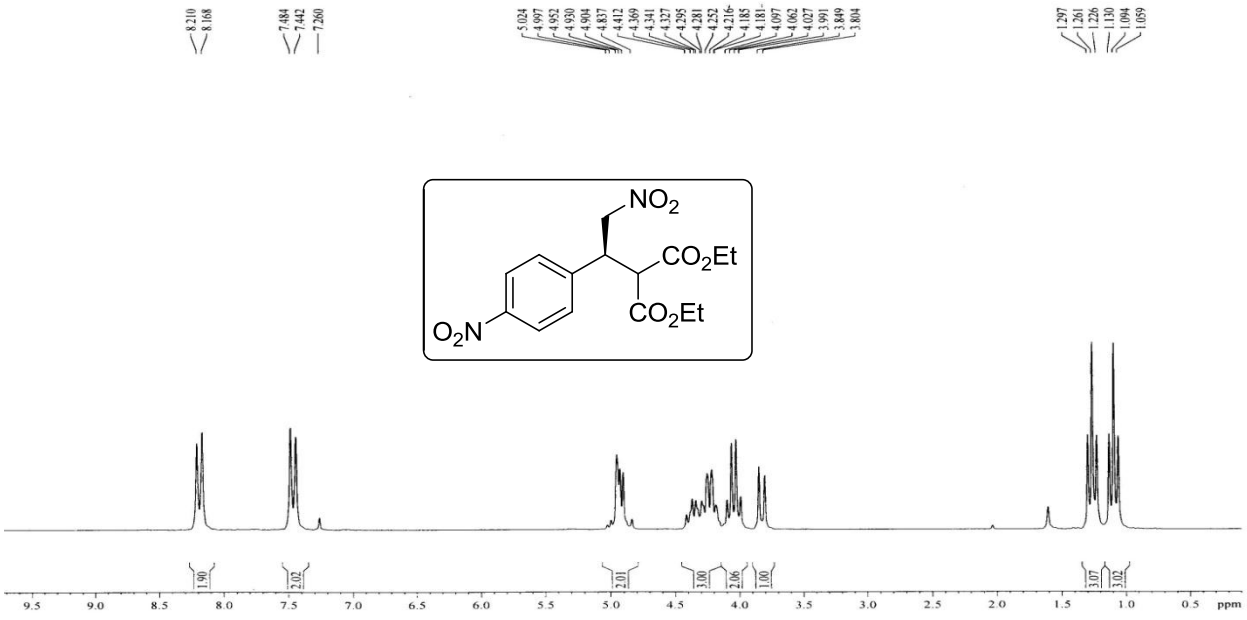
^{13}C NMR Spectrum of compound **6b** (50 MHz, $CDCl_3$).



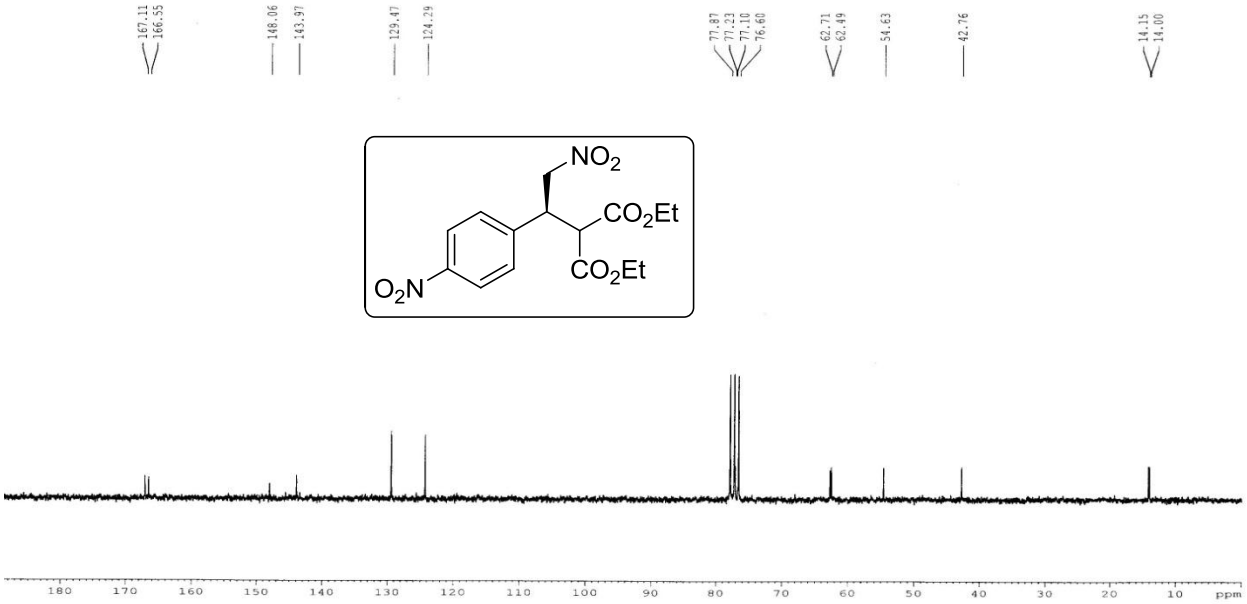
^{1}H NMR Spectrum of compound **6c** (400 MHz, $CDCl_3$)



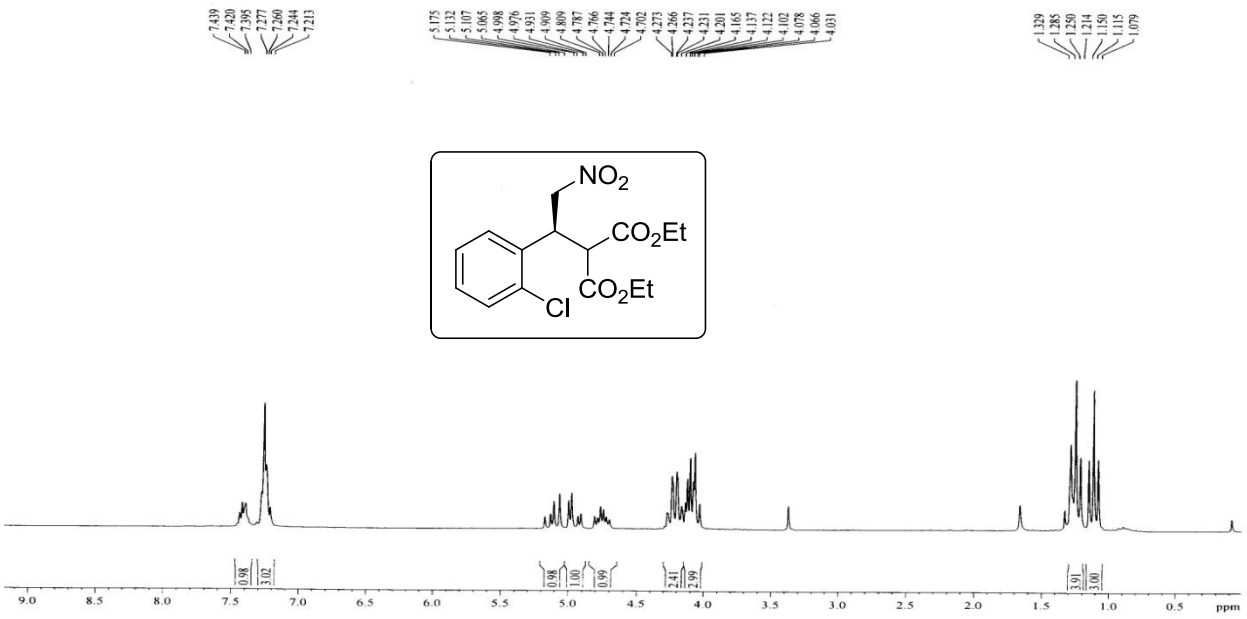
^{13}C NMR Spectrum of compound **6c** (100 MHz, $CDCl_3$).



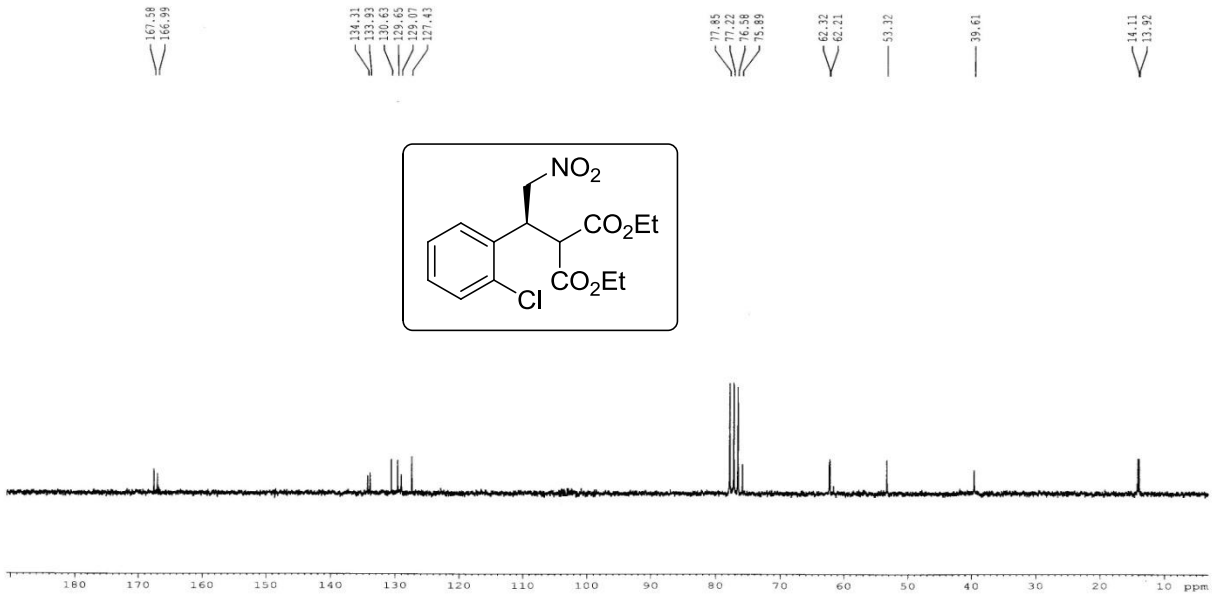
^{1}H NMR Spectrum of compound **6d** (200 MHz, $CDCl_3$)



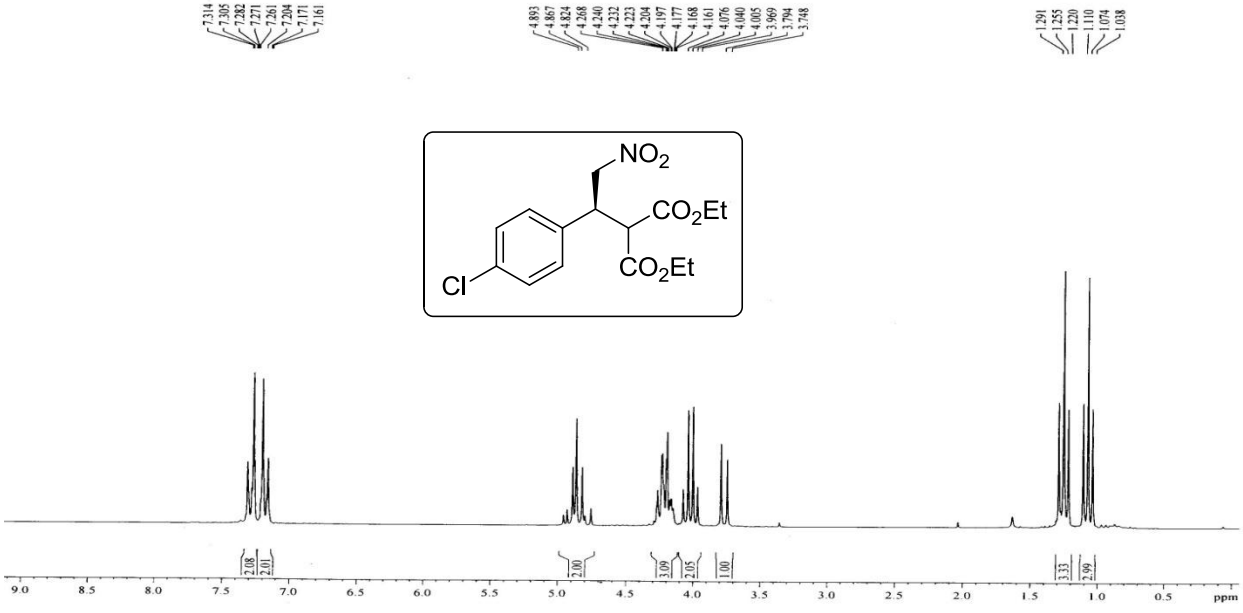
^{13}C NMR Spectrum of compound **6d** (50 MHz, $CDCl_3$).



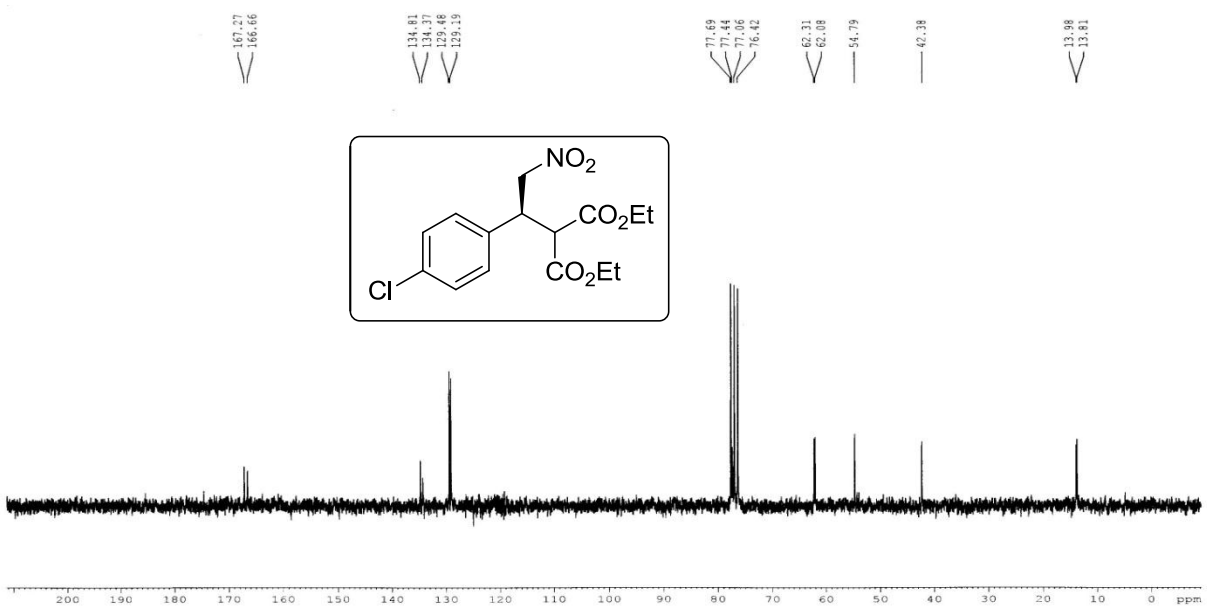
^{1}H NMR Spectrum of compound **6e** (200 MHz, $CDCl_3$)



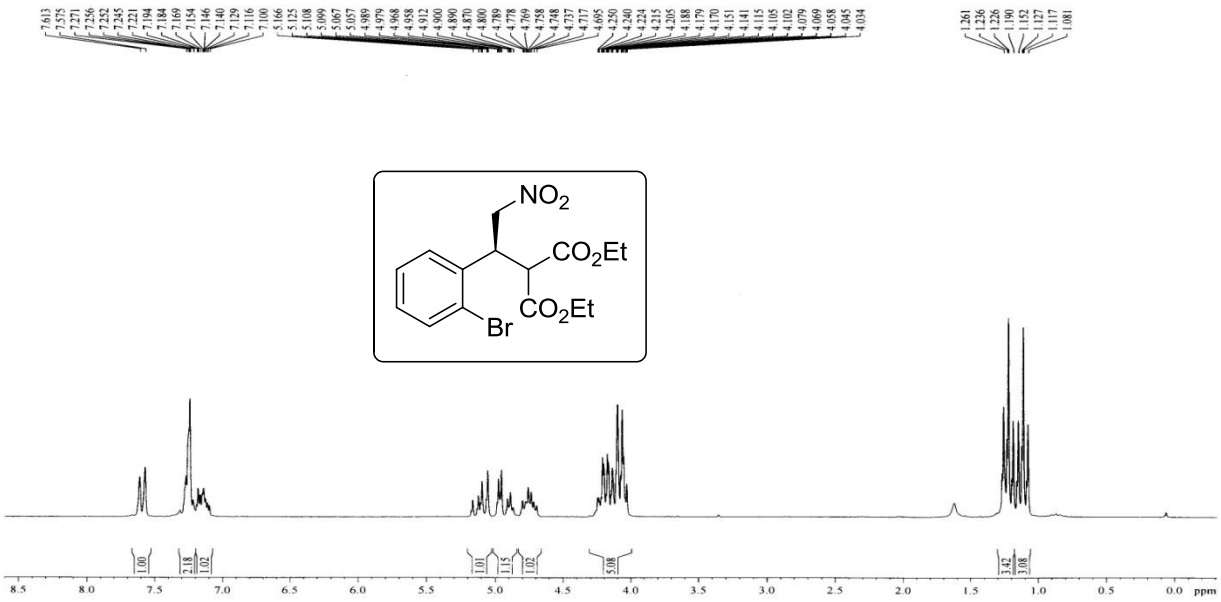
^{13}C NMR Spectrum of compound **6e** (50 MHz, $CDCl_3$).



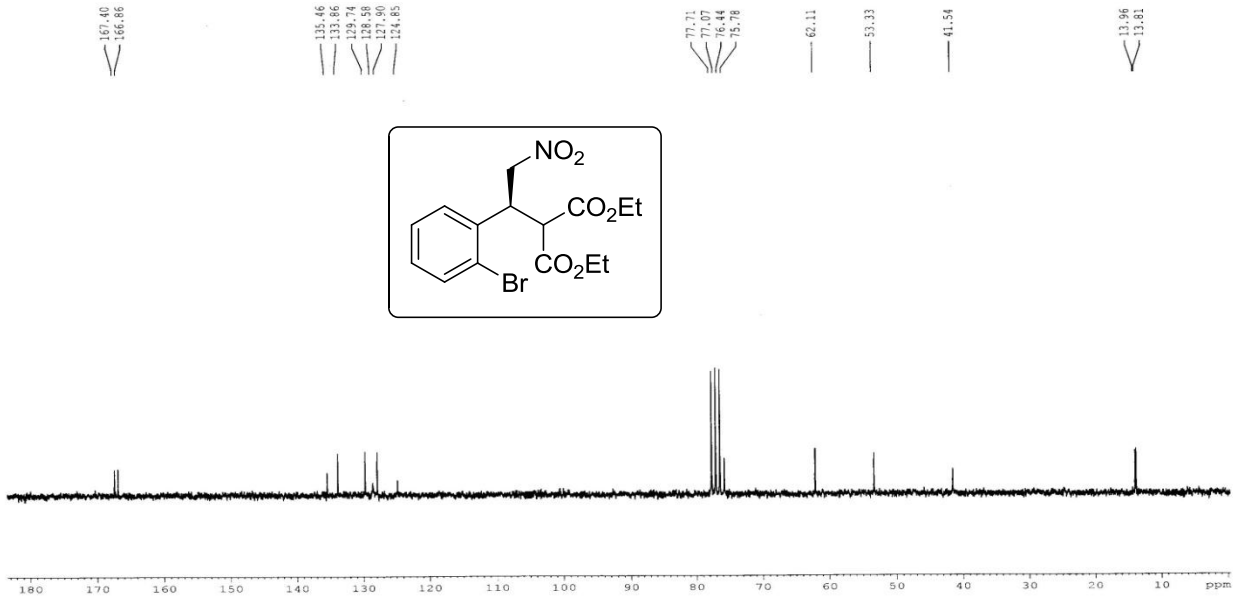
^{1}H NMR Spectrum of compound **6f** (200 MHz, $CDCl_3$)



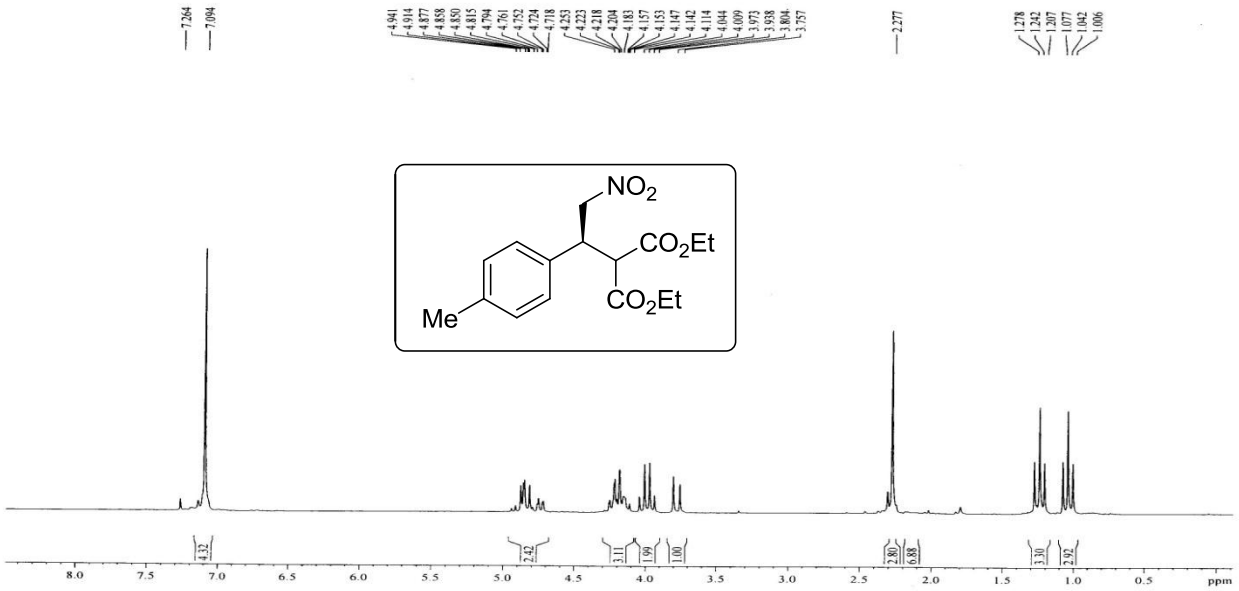
^{13}C NMR Spectrum of compound **6f** (50 MHz, $CDCl_3$).



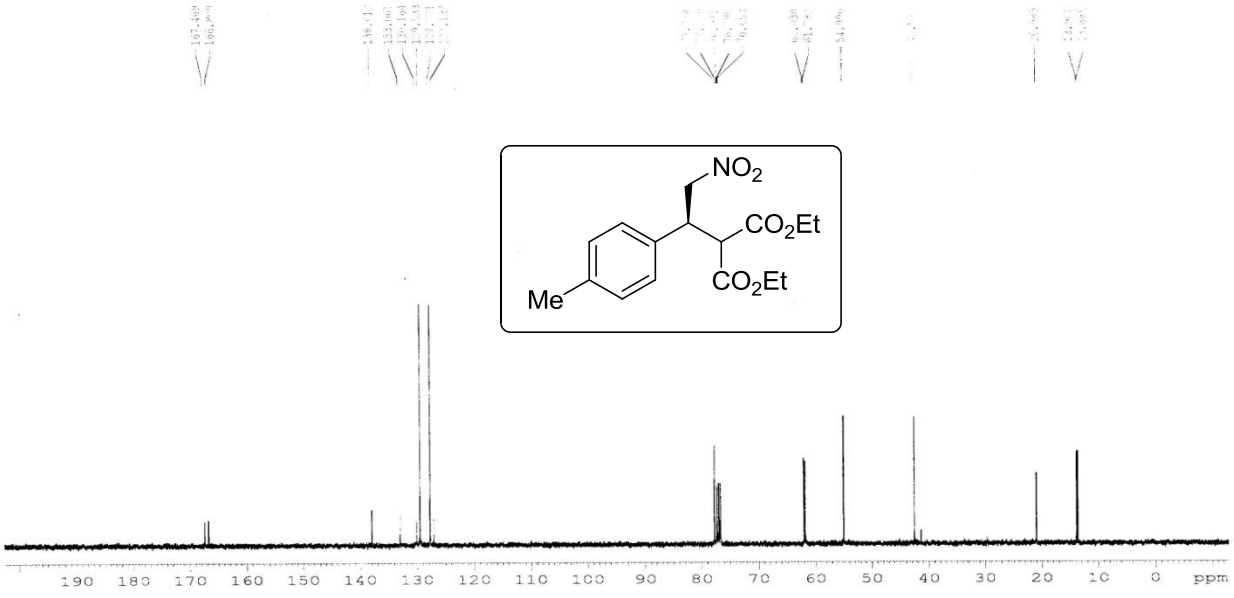
^{1}H NMR Spectrum of compound **6g** (200 MHz, $CDCl_3$)



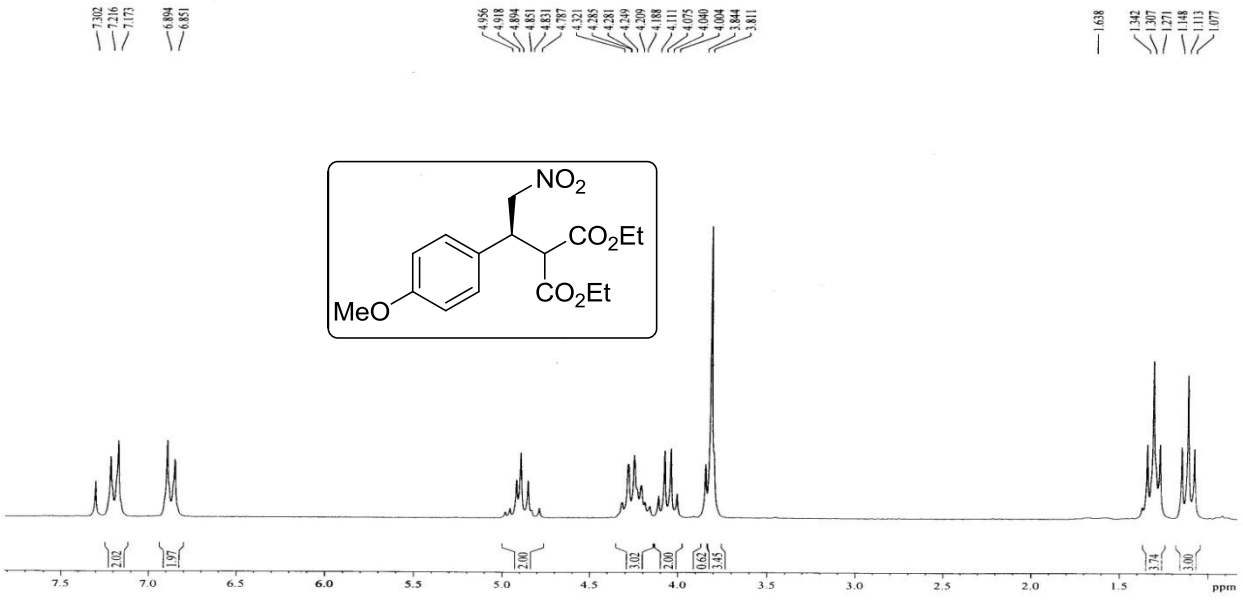
^{13}C NMR Spectrum of compound **6g** (50 MHz, $CDCl_3$).



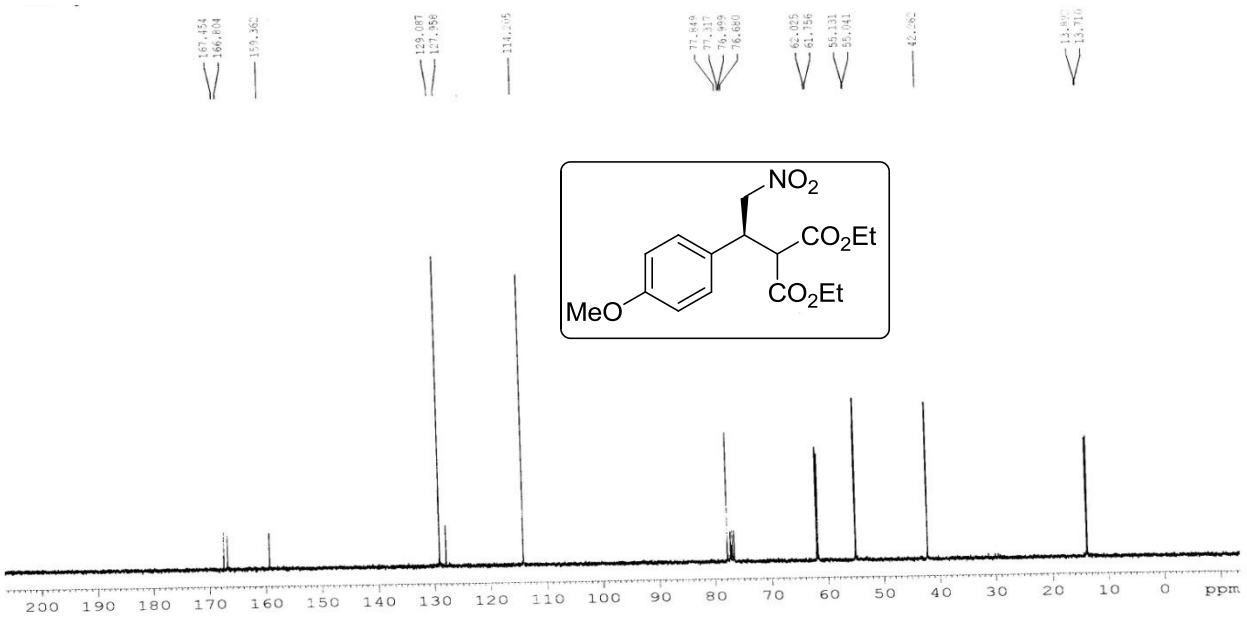
^{1}H NMR Spectrum of compound **6h** (200 MHz, $CDCl_3$)



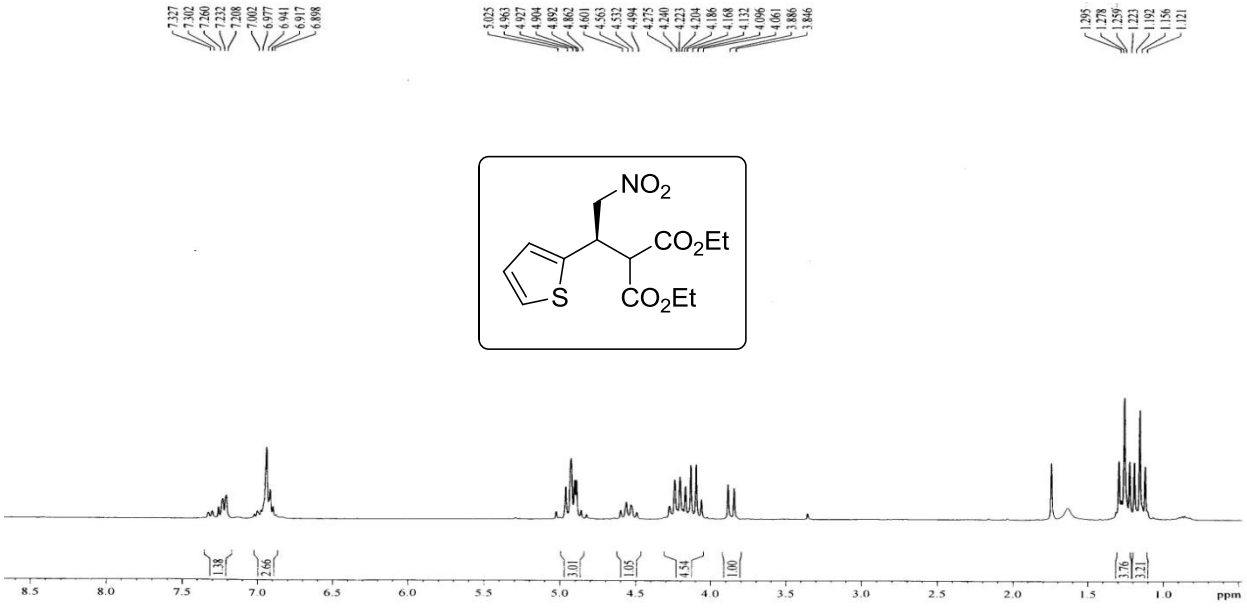
^{13}C NMR Spectrum of compound **6h** (100 MHz, $CDCl_3$).



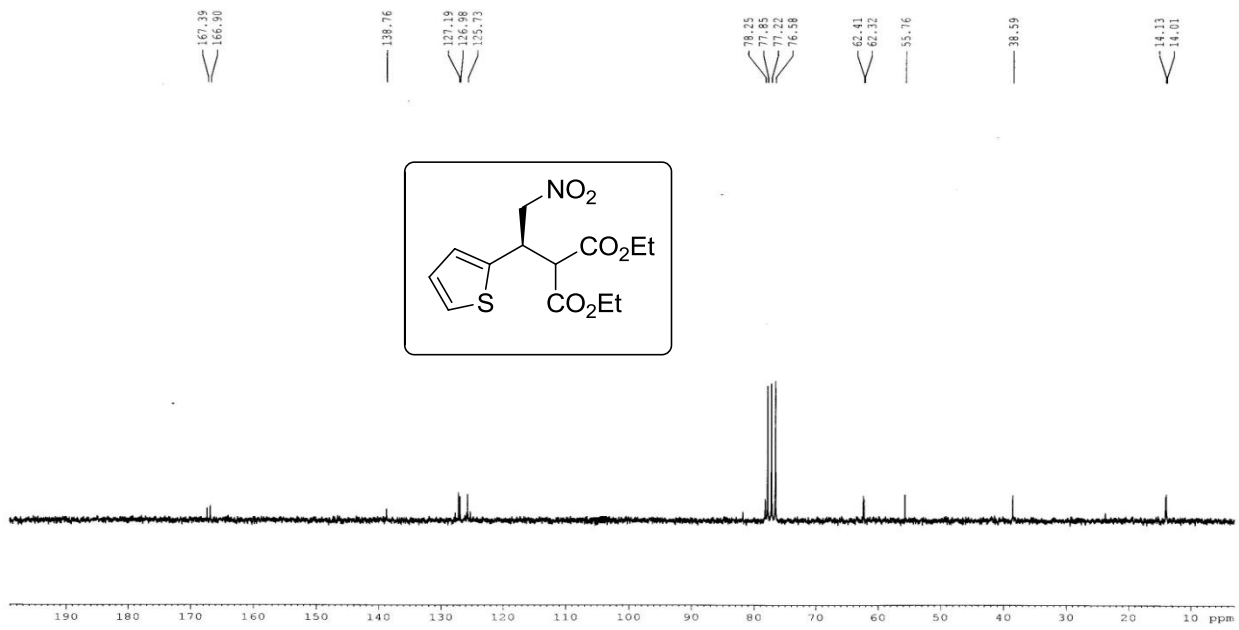
^{1}H NMR Spectrum of compound **6i** (200 MHz, $CDCl_3$)



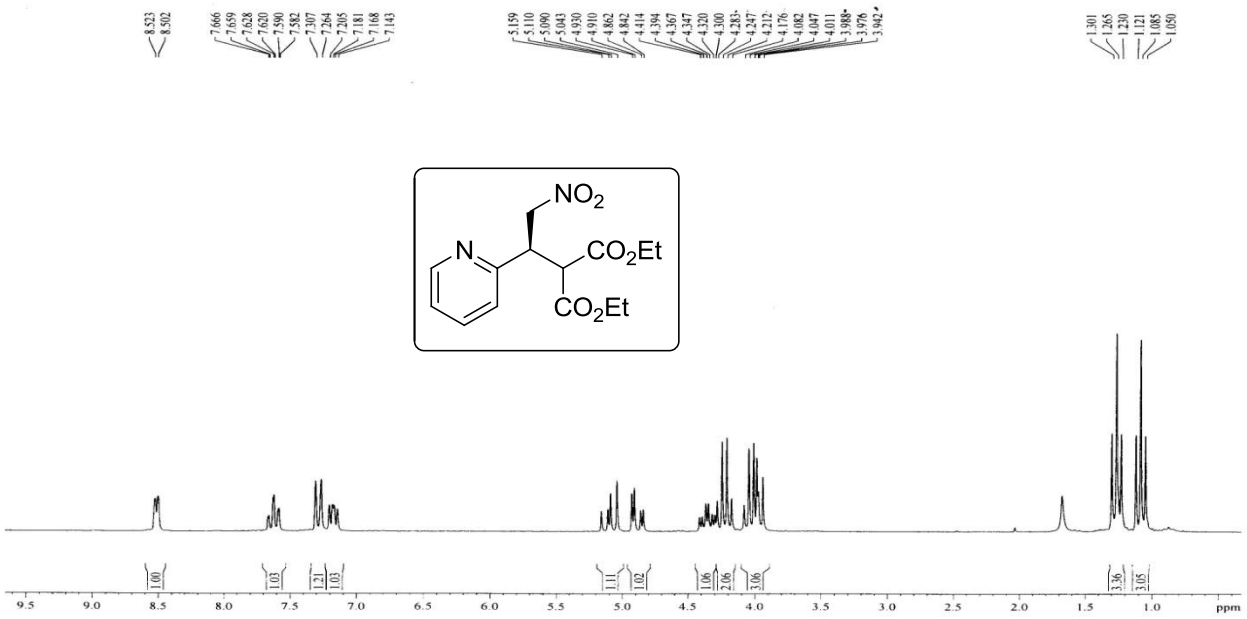
^{13}C NMR Spectrum of compound **6i** (100 MHz, $CDCl_3$).



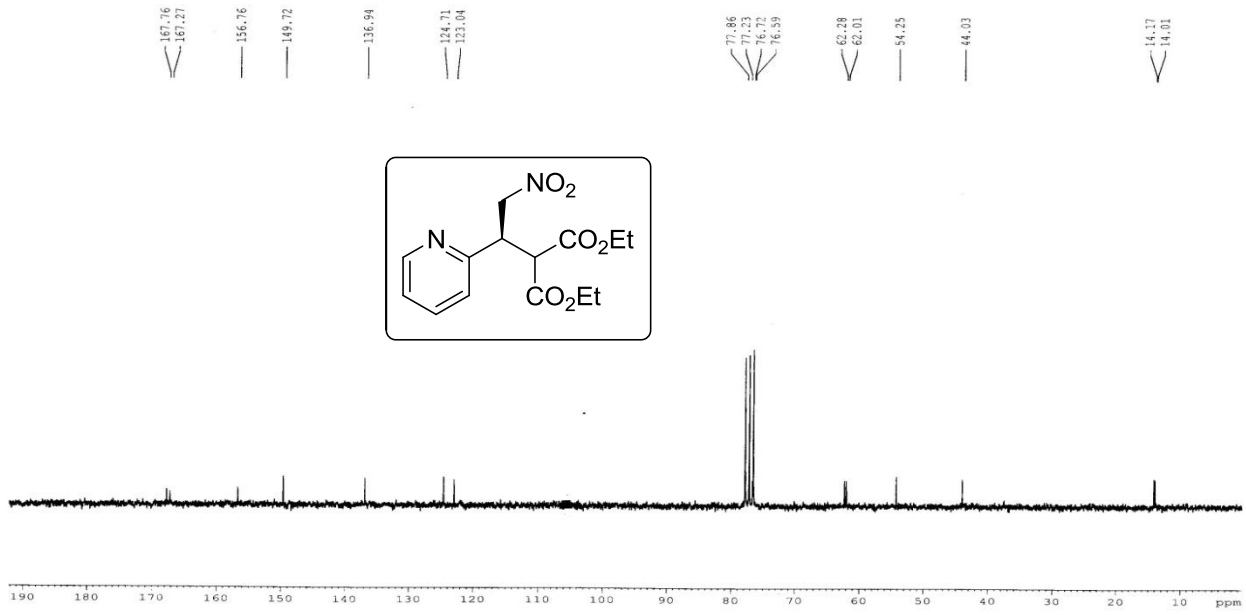
^{1}H NMR Spectrum of compound **6j** (200 MHz, $CDCl_3$)



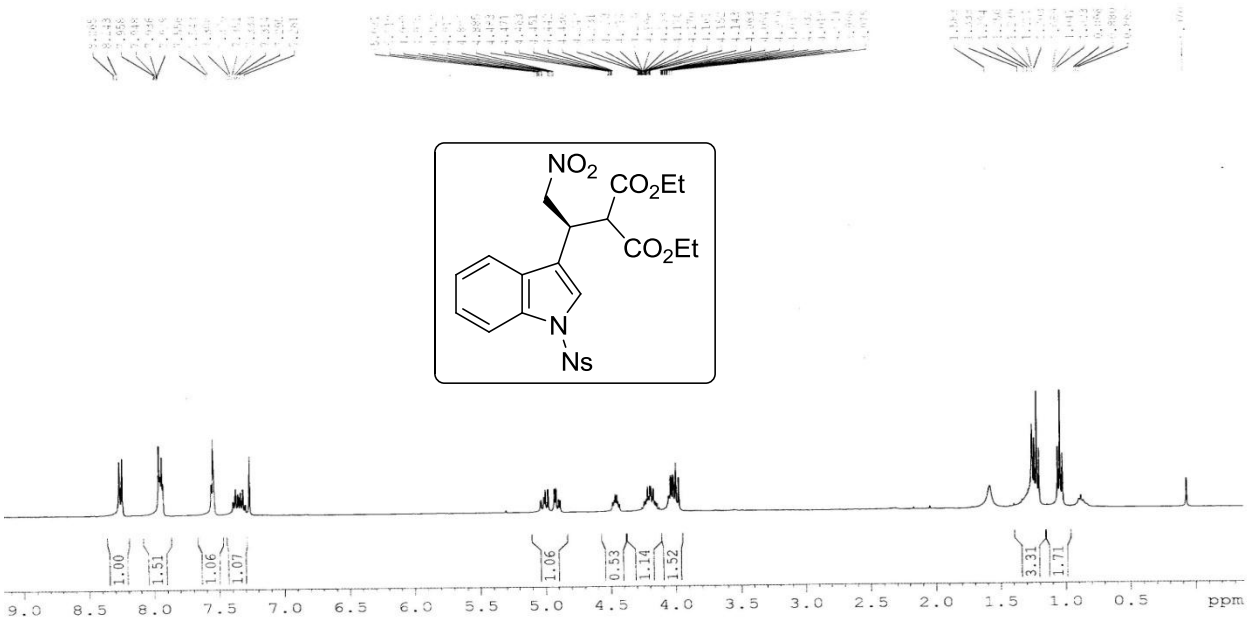
^{13}C NMR Spectrum of compound **6j** (50 MHz, $CDCl_3$).



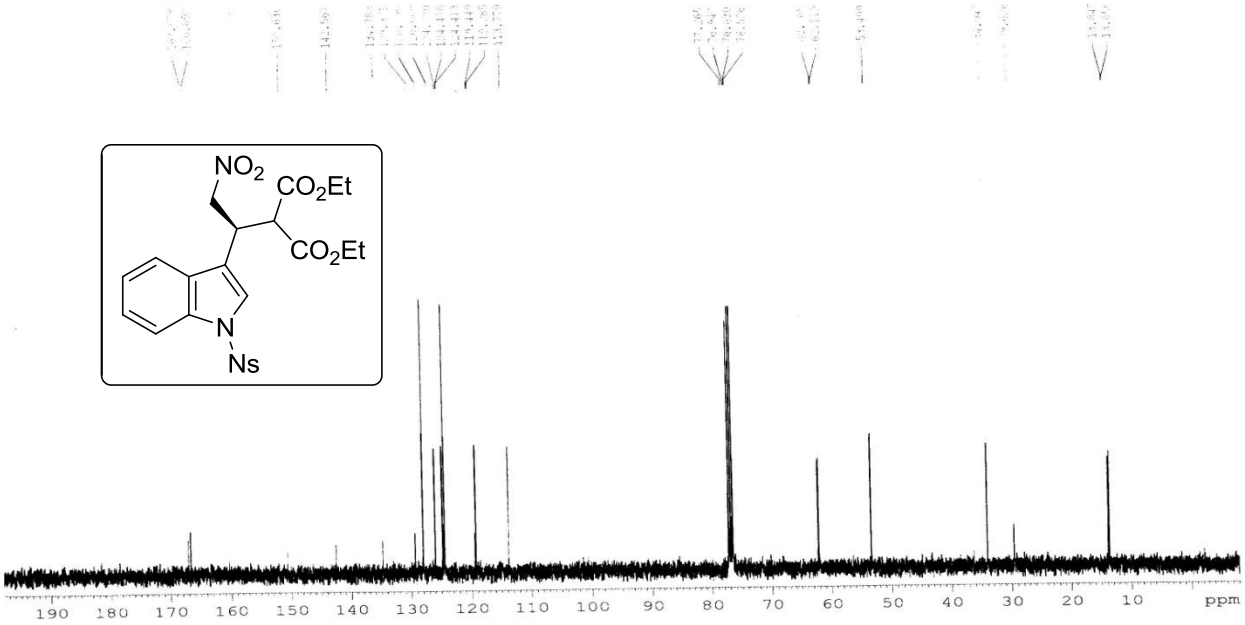
^{1}H NMR Spectrum of compound **6k** (200 MHz, $CDCl_3$)



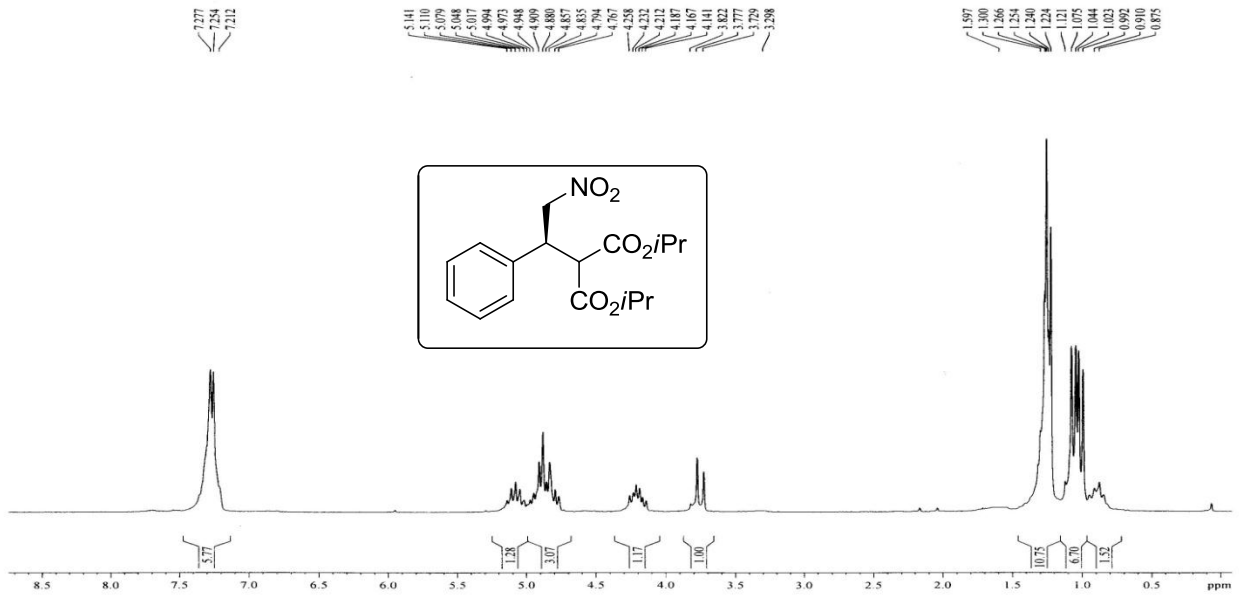
^{13}C NMR Spectrum of compound **6k** (50 MHz, $CDCl_3$).



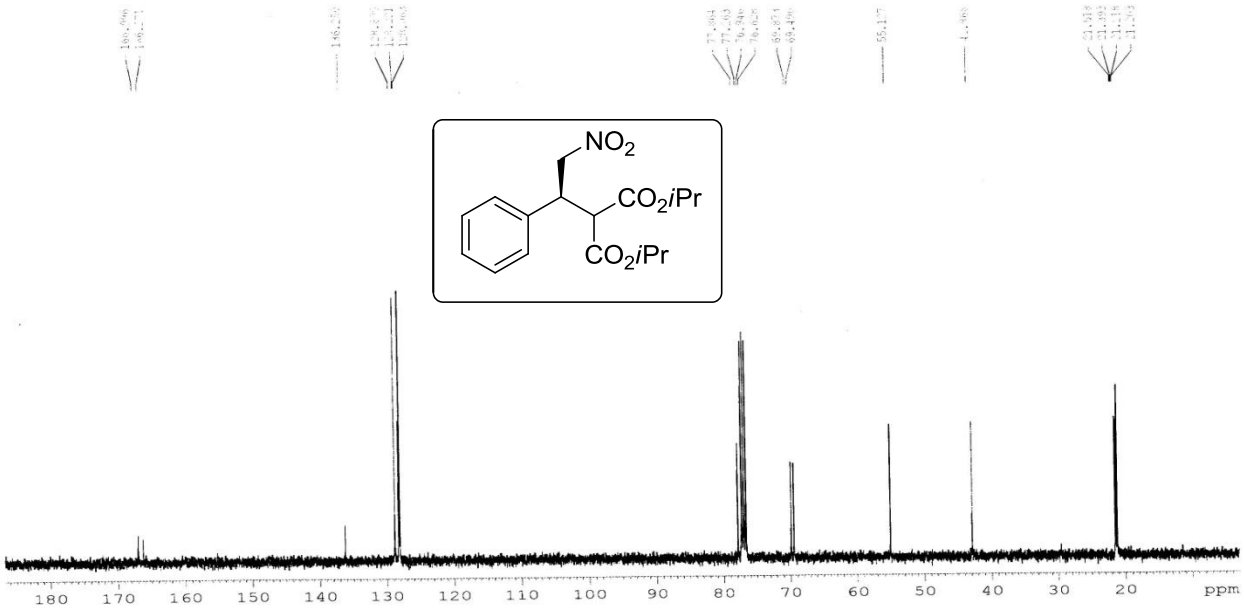
^{1}H NMR Spectrum of compound **6l** (400 MHz, $CDCl_3$)



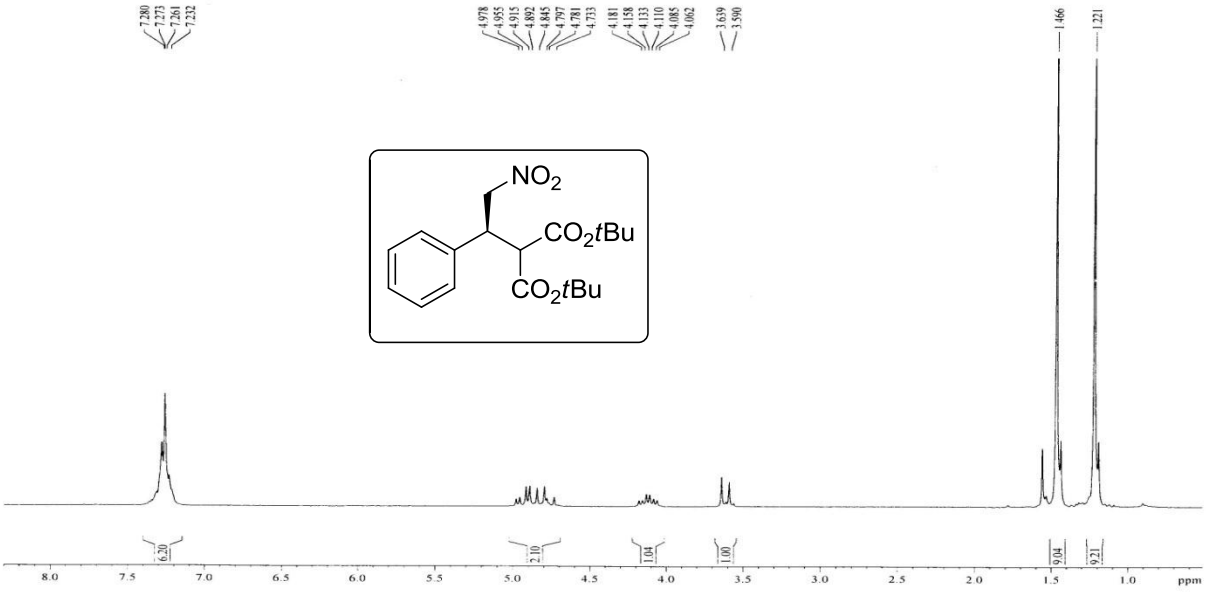
^{13}C NMR Spectrum of compound **6l** (100 MHz, $CDCl_3$).



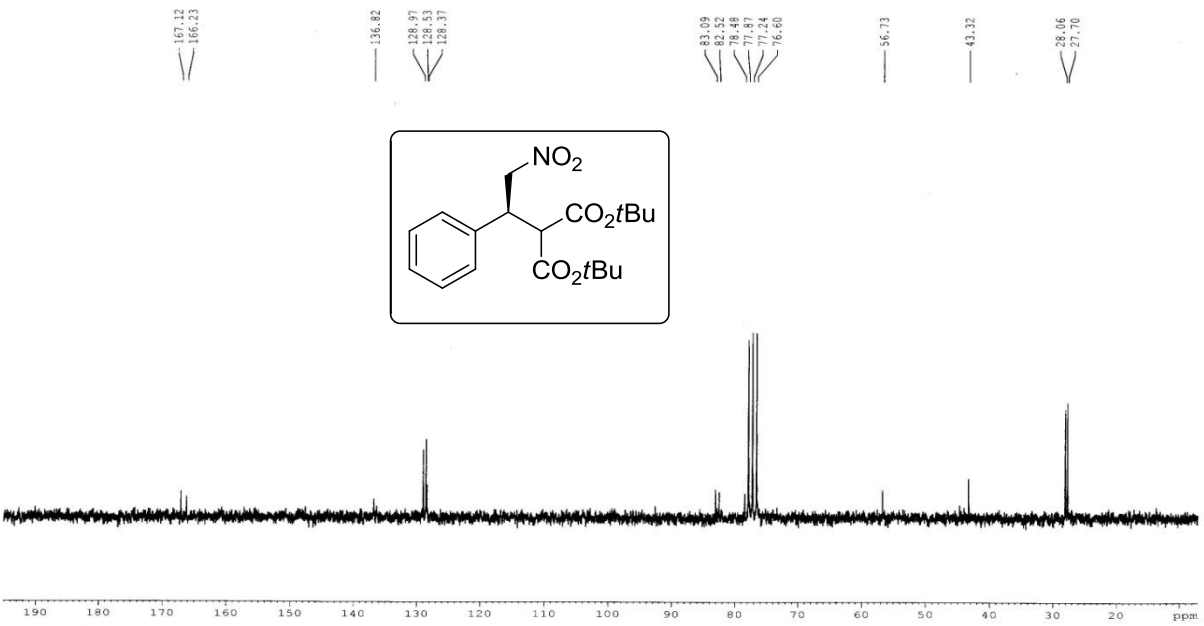
^{1}H NMR Spectrum of compound **6-isopropyl** (200 MHz, $CDCl_3$)



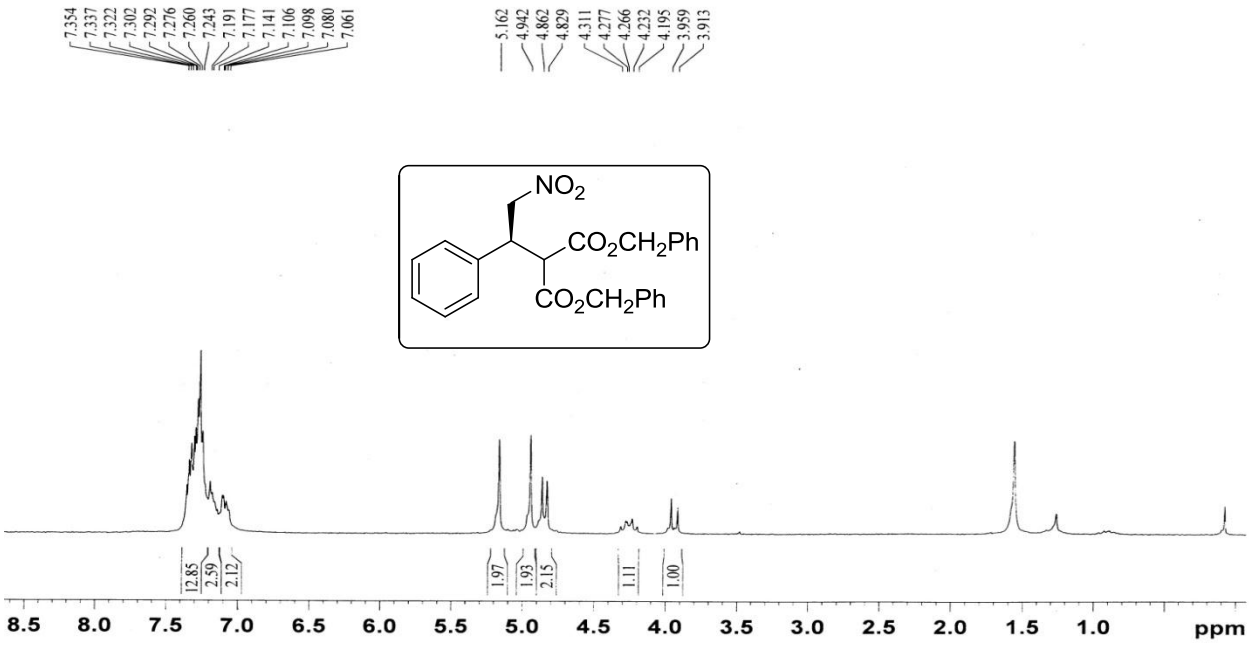
^{13}C NMR Spectrum of compound **6-isopropyl** (100 MHz, $CDCl_3$).



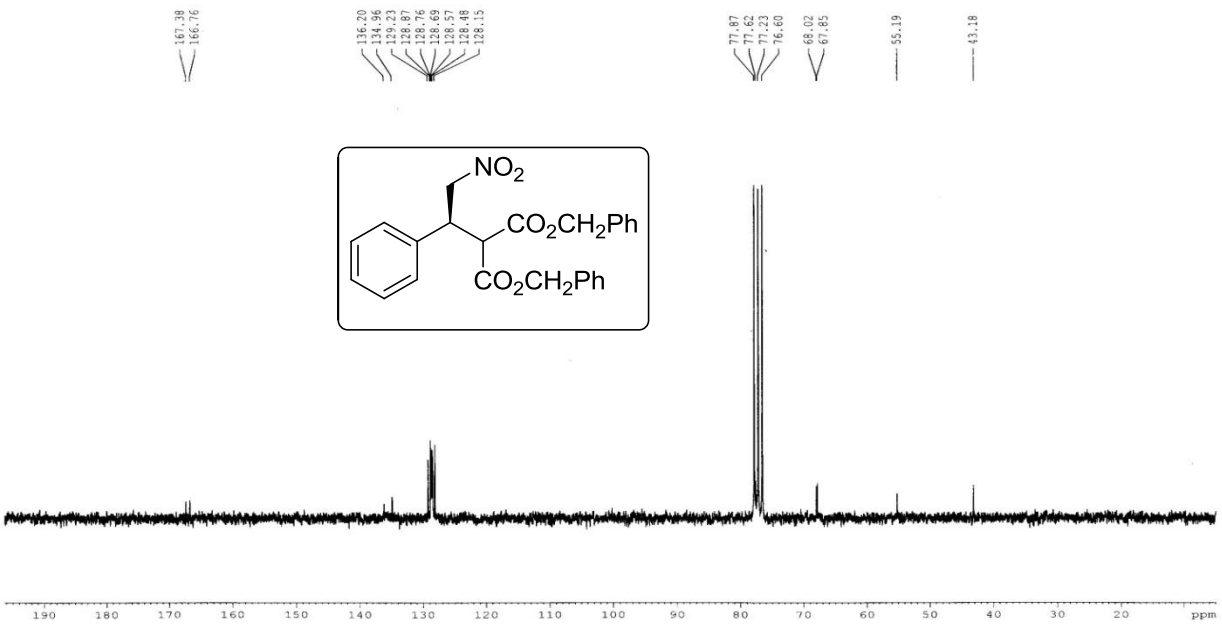
^{1}H NMR Spectrum of compound **6-tertbutyl** (200 MHz, $CDCl_3$)



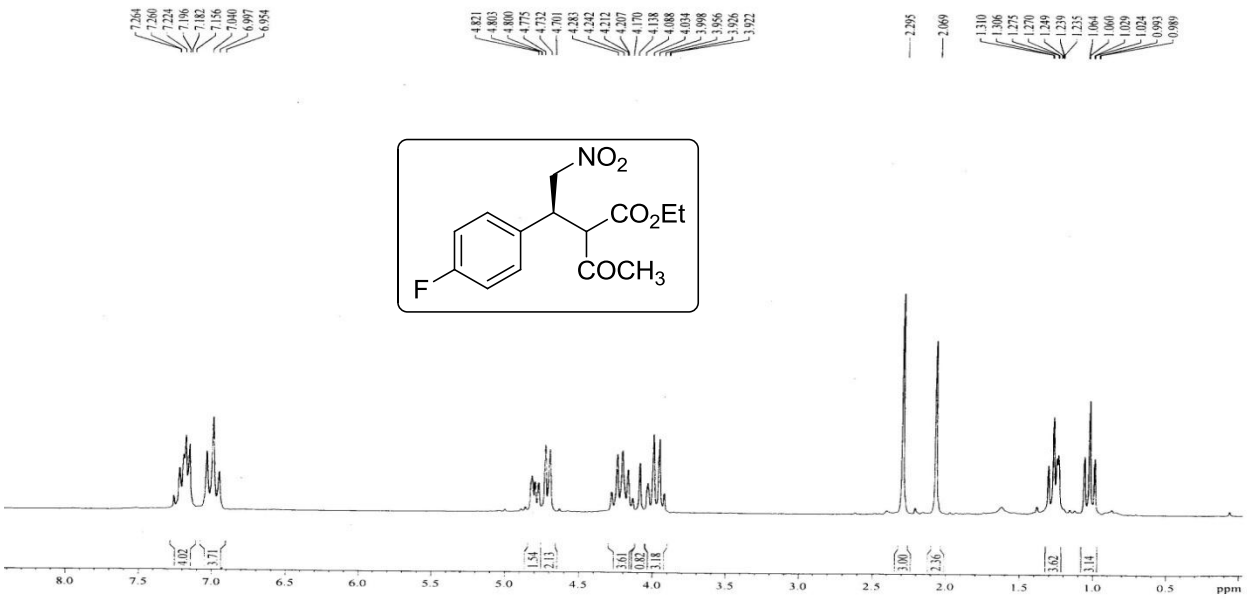
^{13}C NMR Spectrum of compound **6-tertbutyl** (50 MHz, $CDCl_3$).



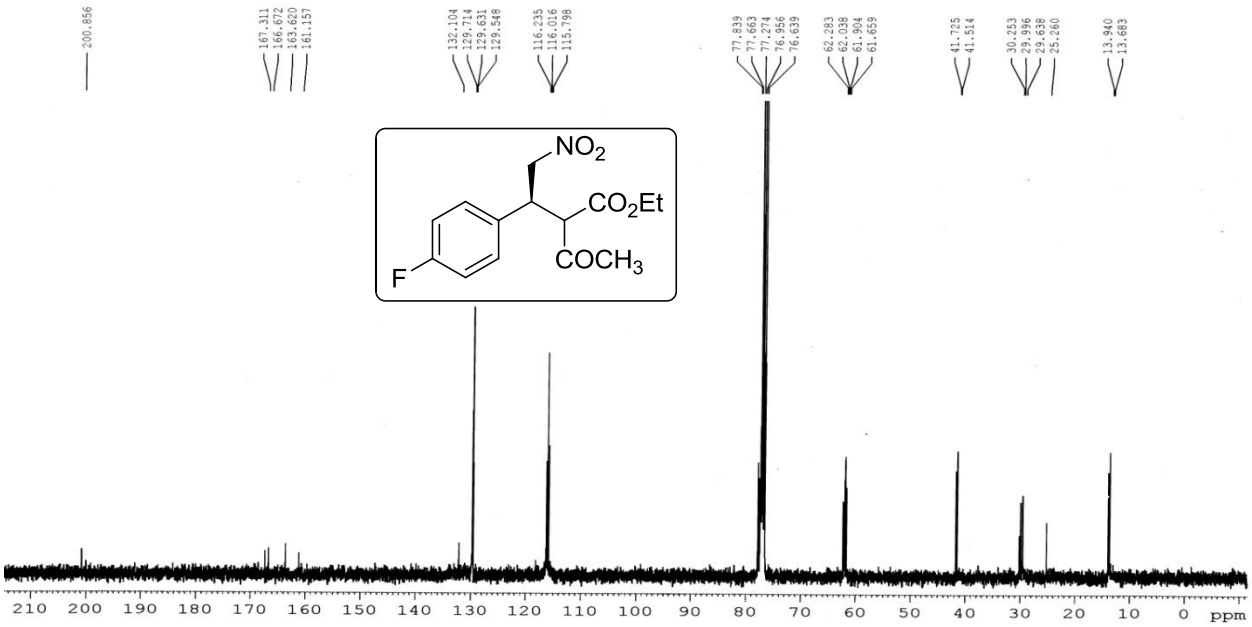
^{1}H NMR Spectrum of compound **6-dibenzyl** (200 MHz, $CDCl_3$)



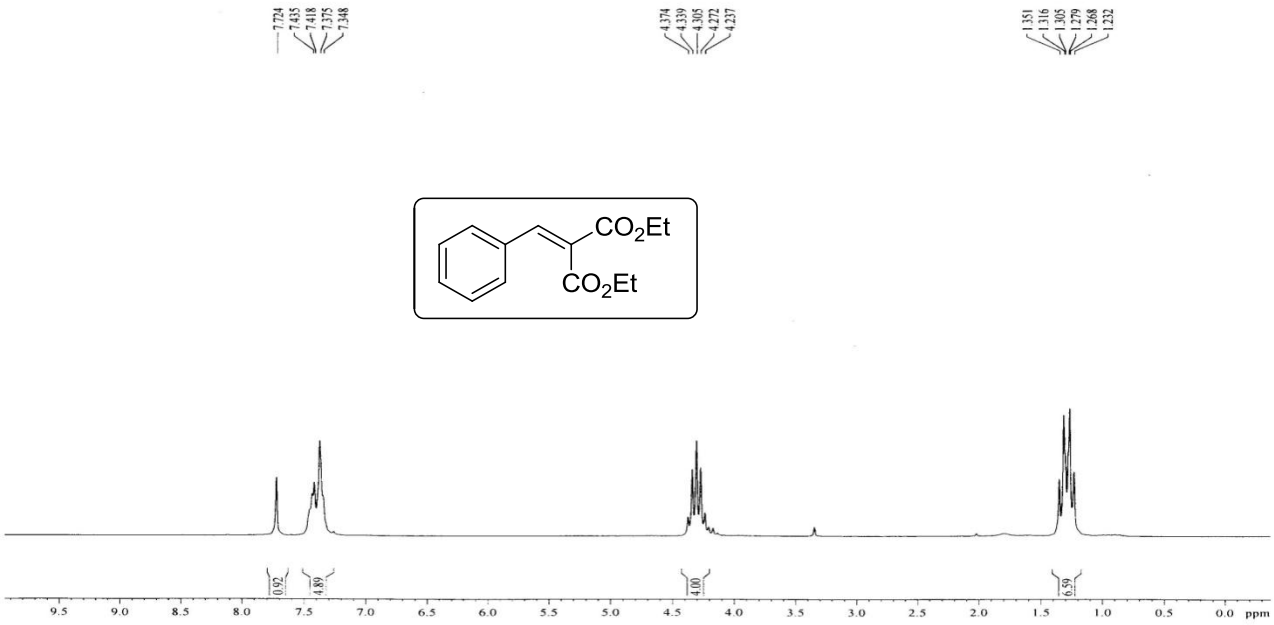
^{13}C NMR Spectrum of compound **6-dibenzyl** (50 MHz, $CDCl_3$).



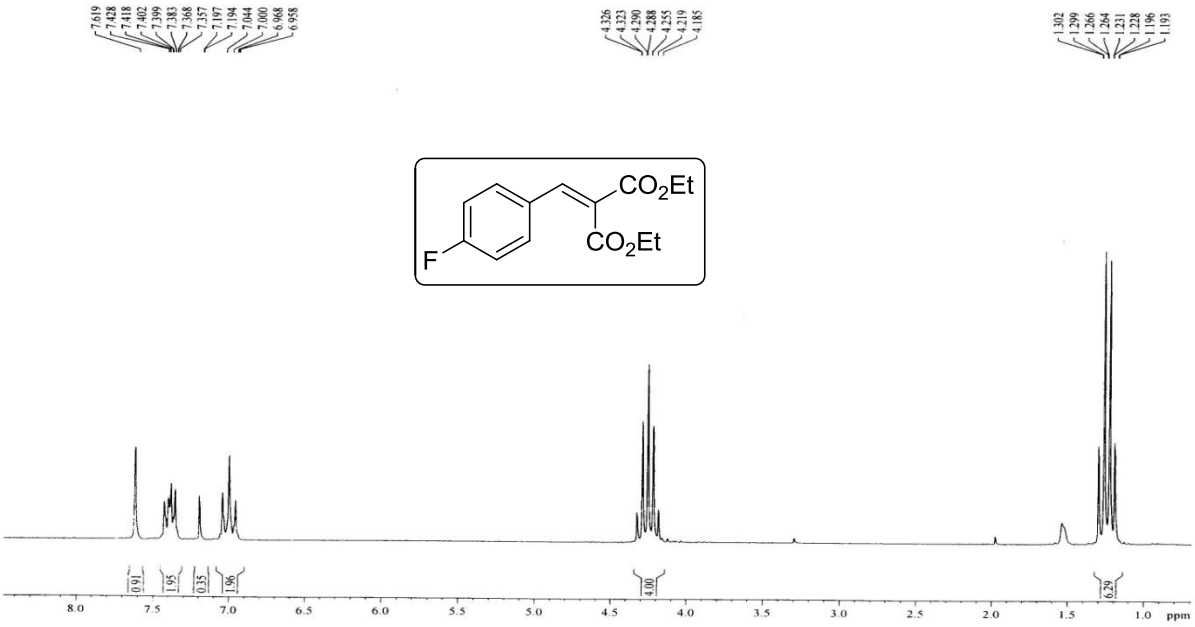
^{1}H NMR Spectrum of compound **8** (200 MHz, $CDCl_3$)



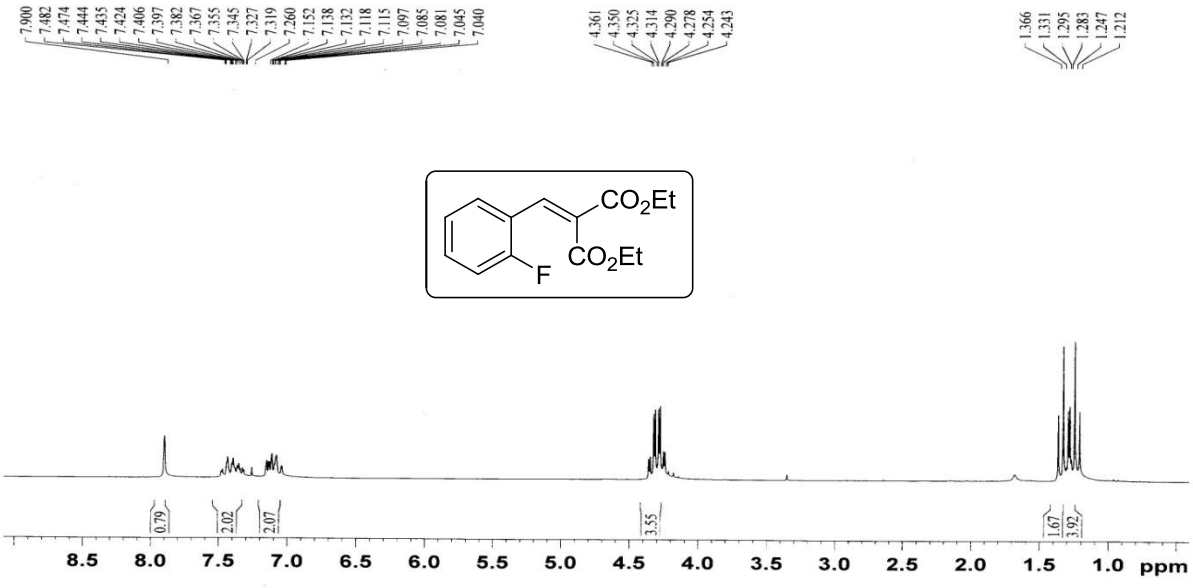
^{13}C NMR Spectrum of compound **8** (50 MHz, $CDCl_3$).



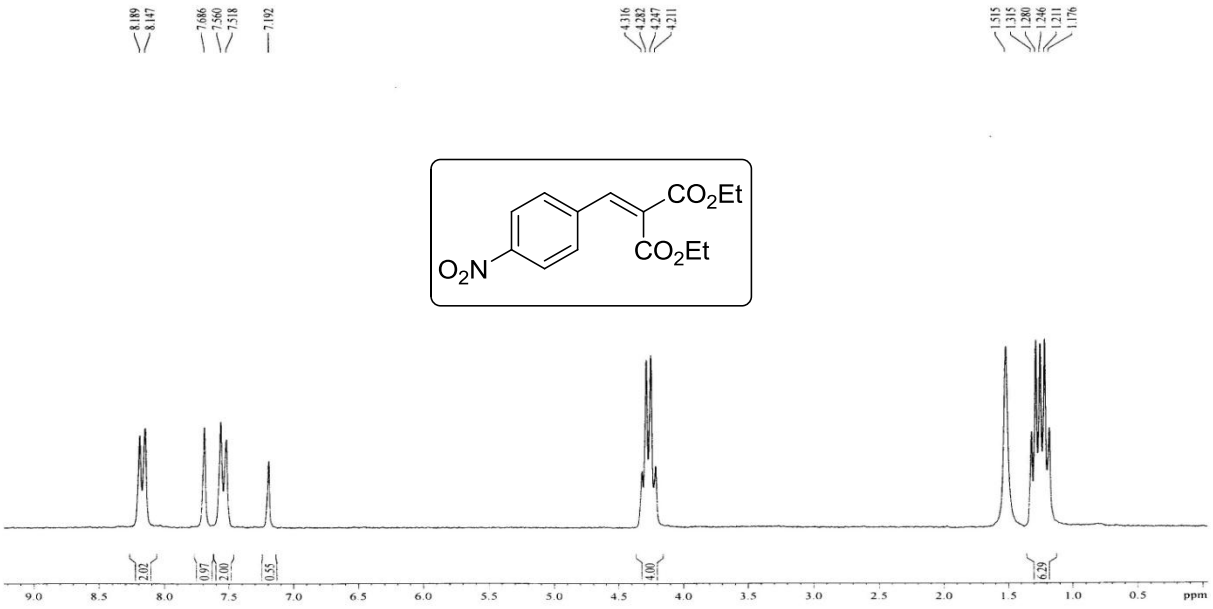
^{1}H NMR Spectrum of compound **5a** (200 MHz, $CDCl_3$)



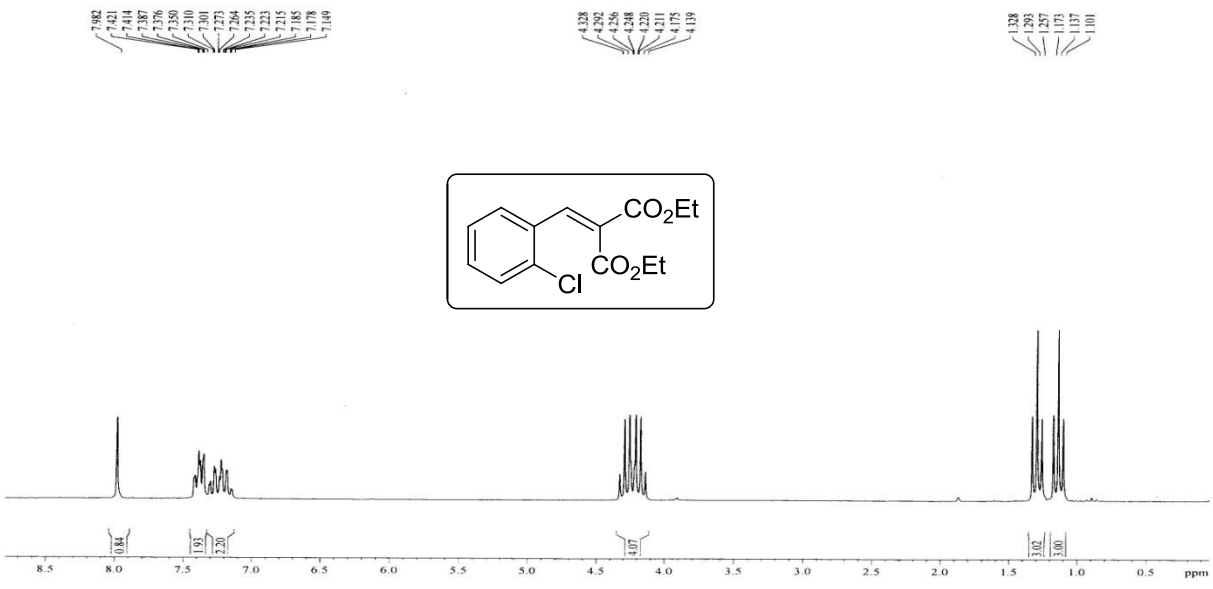
^{1}H NMR Spectrum of compound **5b** (200 MHz, $CDCl_3$)



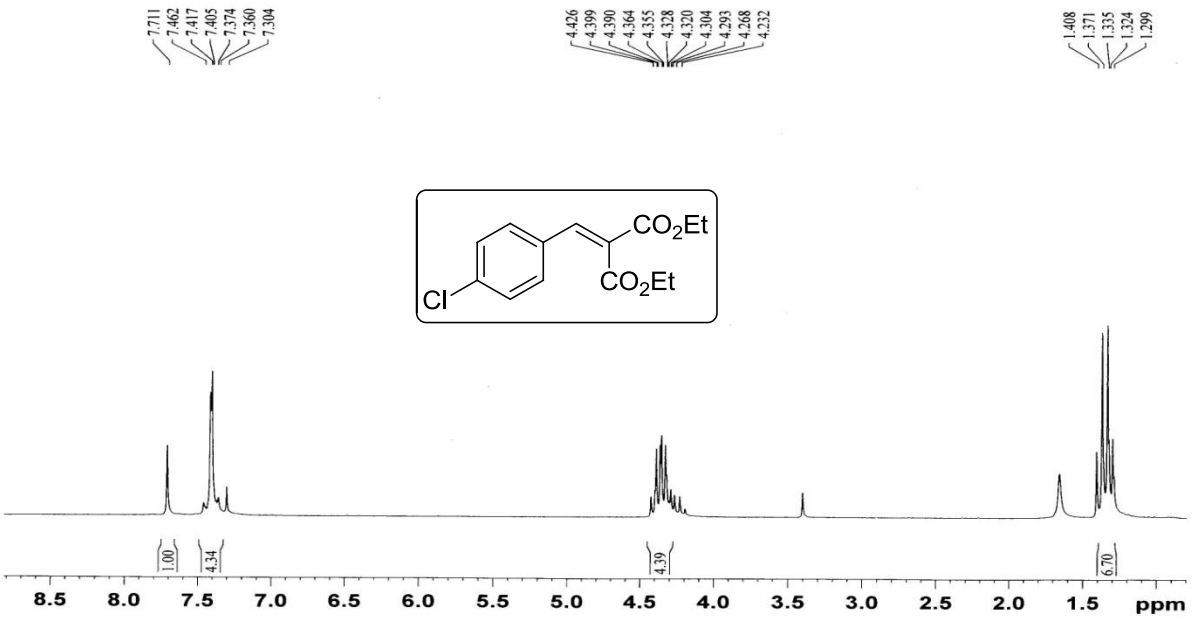
^{1}H NMR Spectrum of compound **5c** (200 MHz, $CDCl_3$)



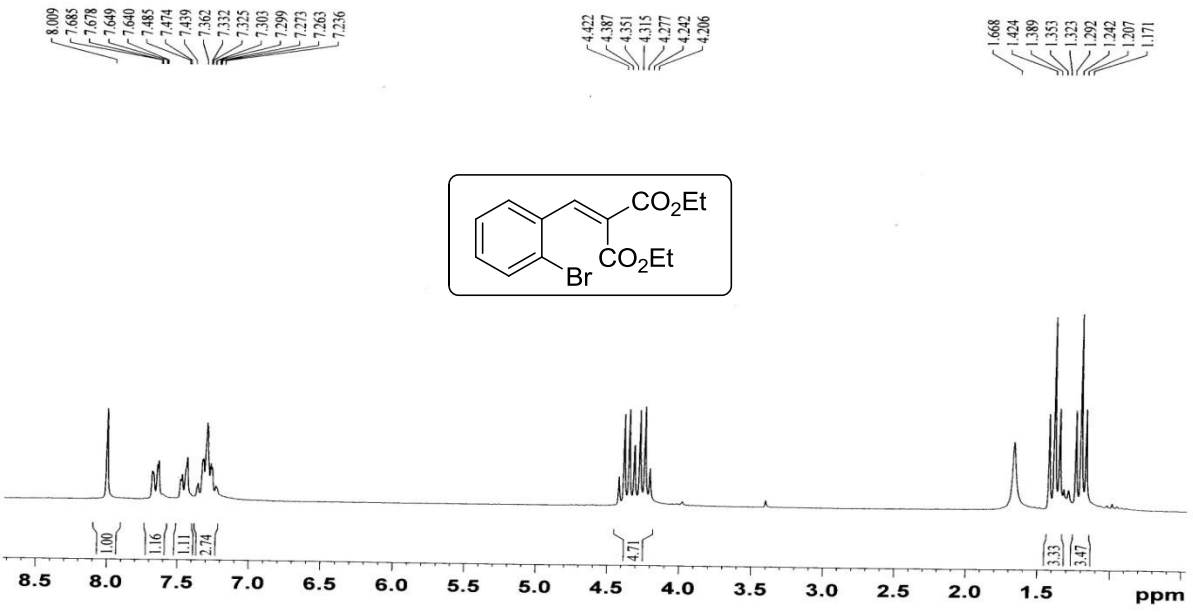
^{1}H NMR Spectrum of compound **5d** (200 MHz, $CDCl_3$)



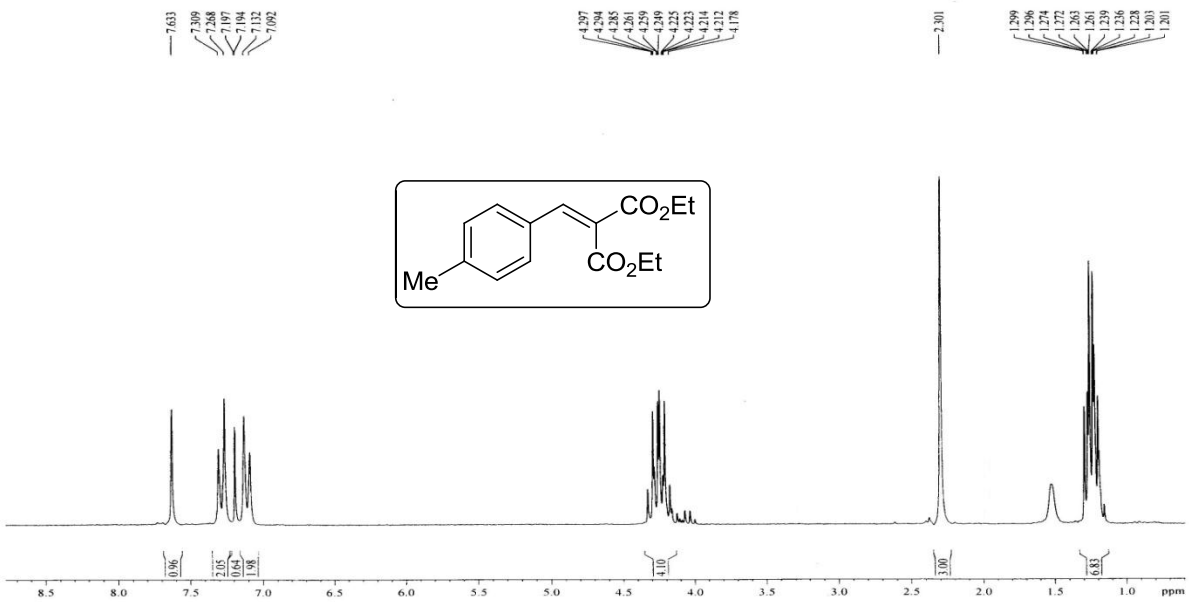
^{1}H NMR Spectrum of compound **5e** (200 MHz, $CDCl_3$)



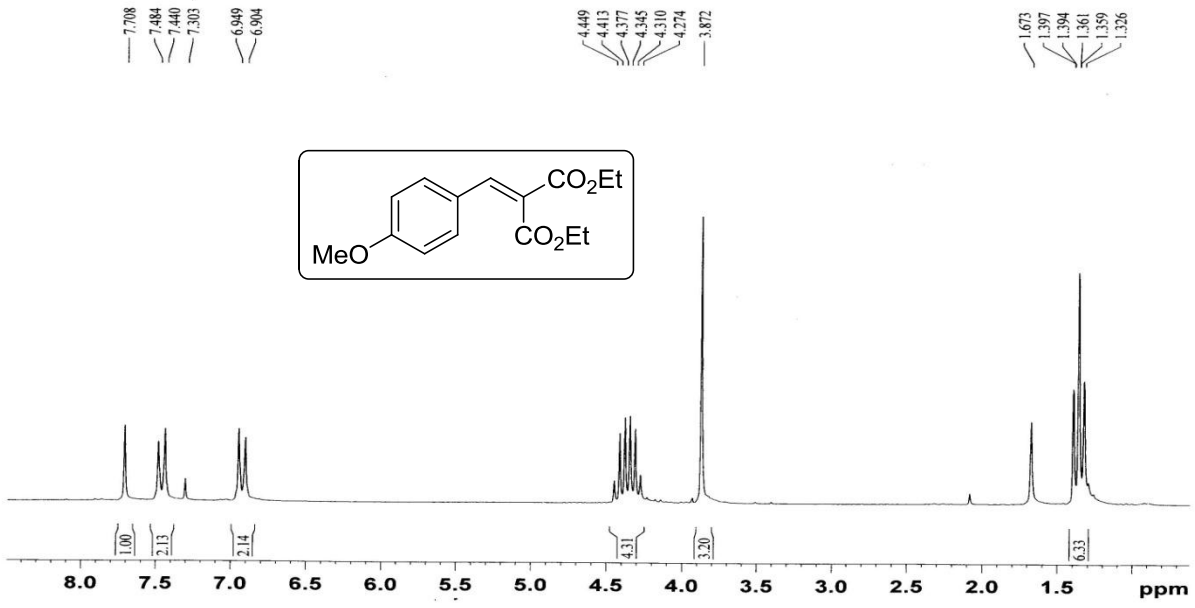
^{1}H NMR Spectrum of compound **5f** (200 MHz, $CDCl_3$)



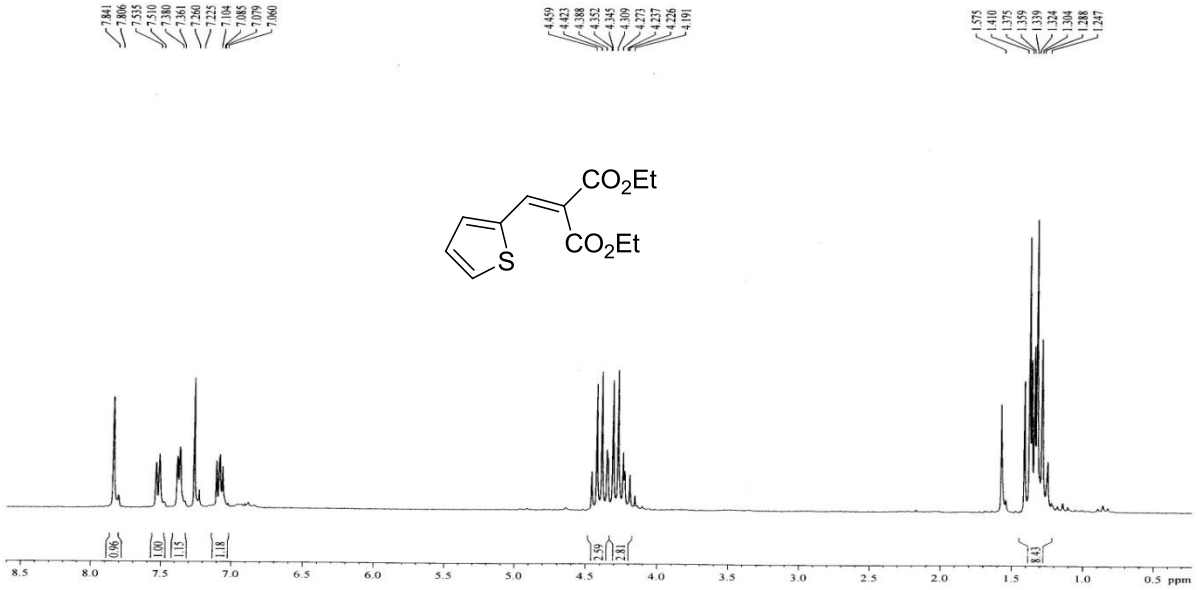
^{1}H NMR Spectrum of compound **5g** (200 MHz, $CDCl_3$)



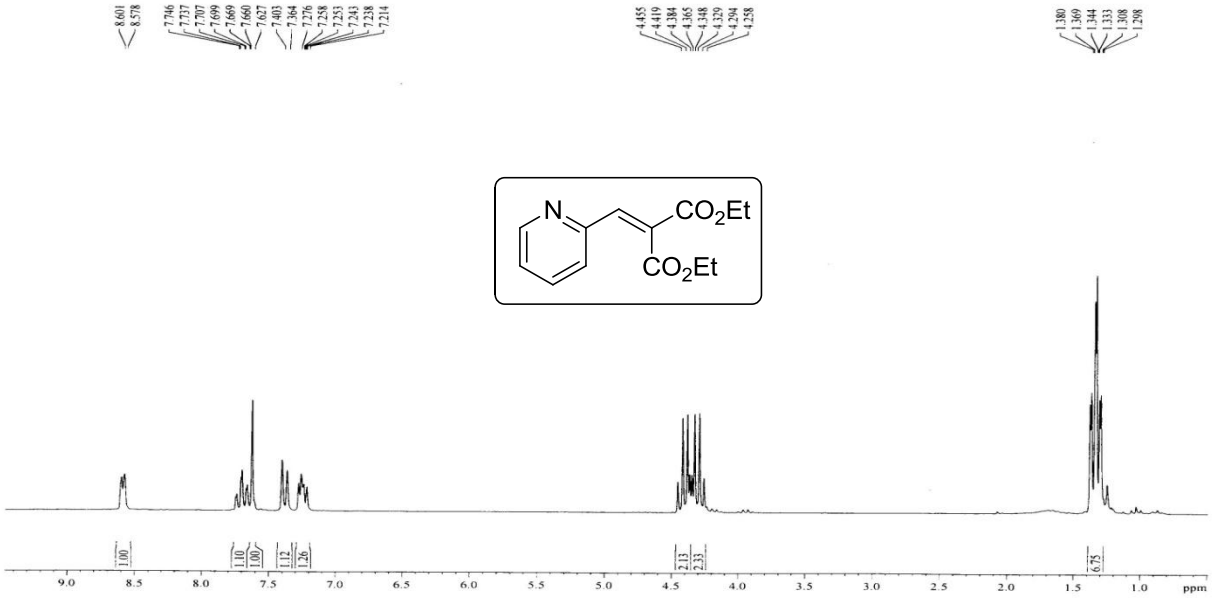
^{1}H NMR Spectrum of compound **5h** (200 MHz, $CDCl_3$)



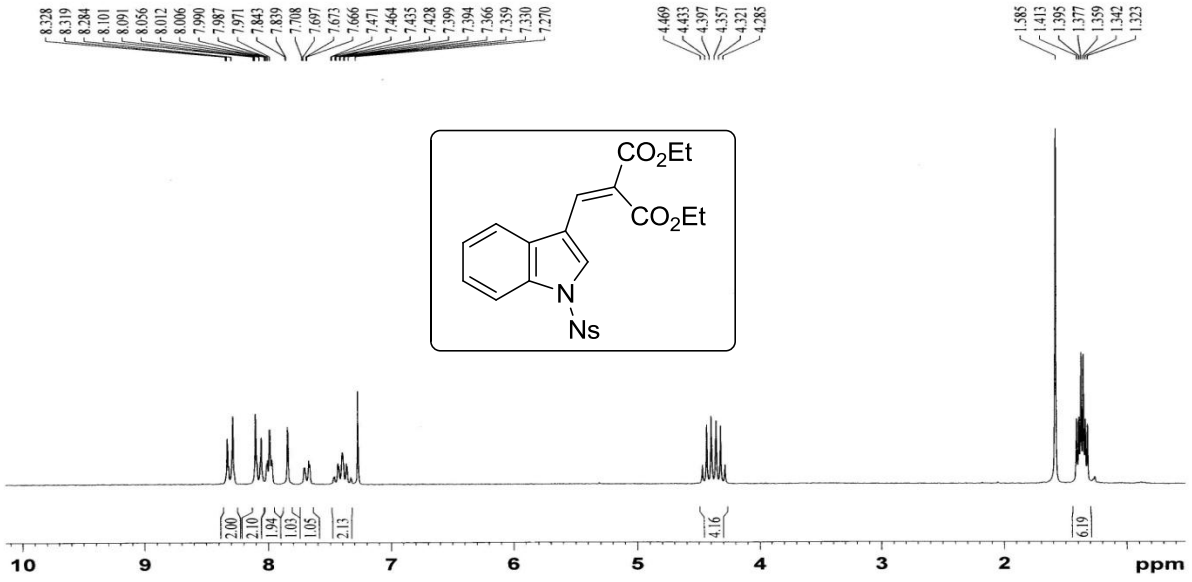
^{1}H NMR Spectrum of compound **5i** (200 MHz, $CDCl_3$)



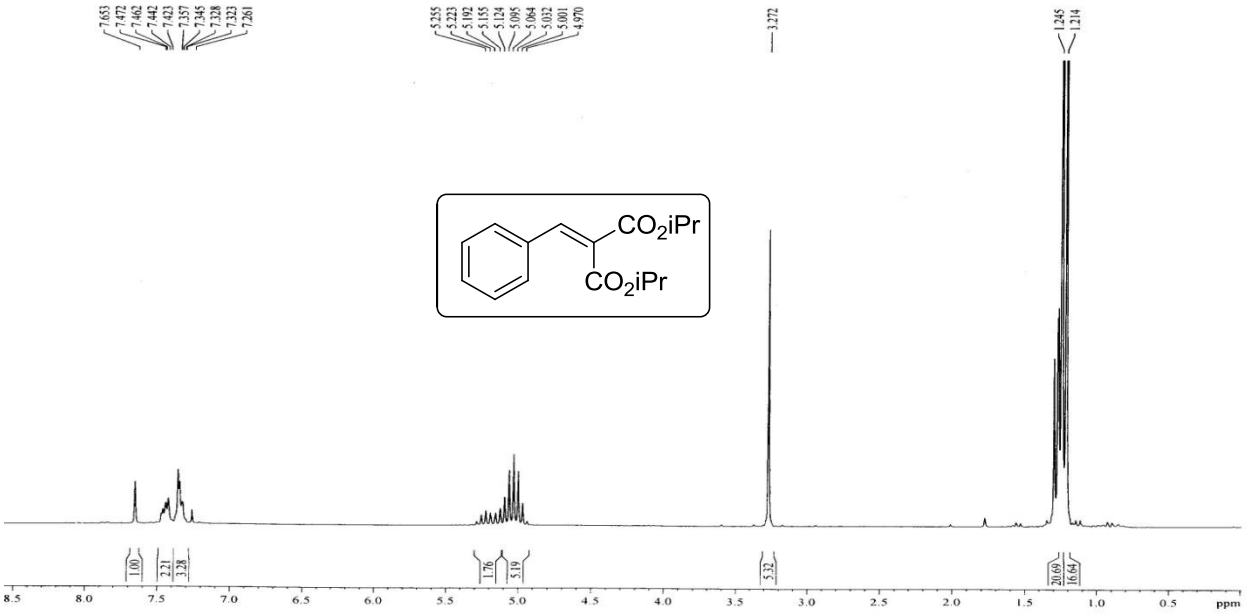
^{1}H NMR Spectrum of compound **5j** (200 MHz, $CDCl_3$)



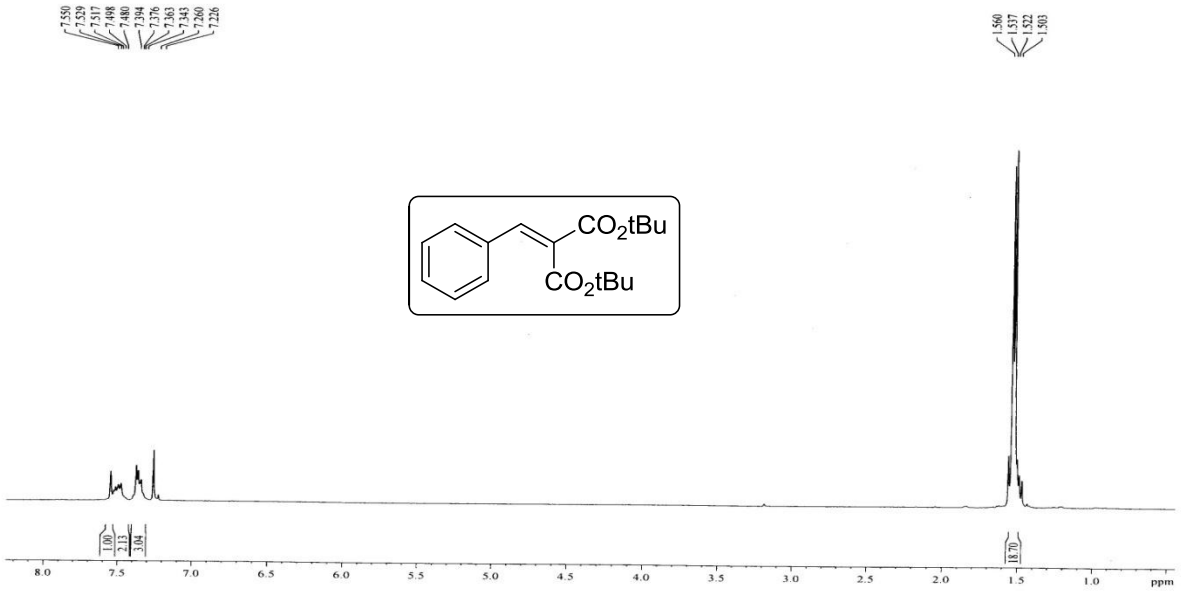
^{1}H NMR Spectrum of compound **5k** (200 MHz, $CDCl_3$)



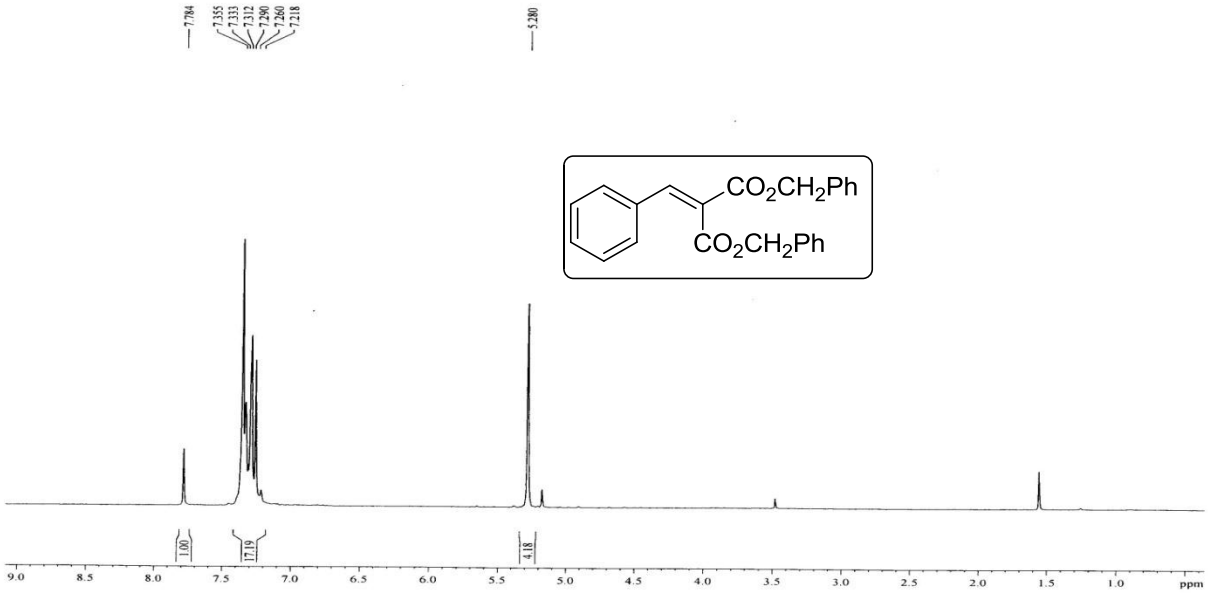
^{1}H NMR Spectrum of compound **5l** (200 MHz, $CDCl_3$)



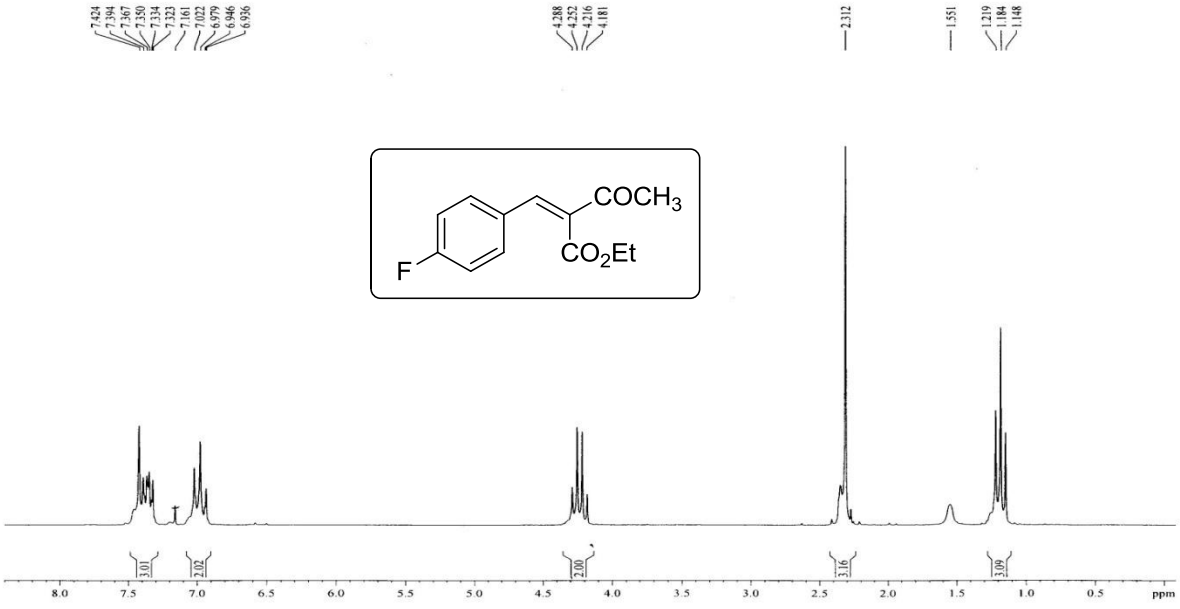
^{1}H NMR Spectrum of compound **5-isopropyl** (200 MHz, $CDCl_3$)



^{1}H NMR Spectrum of compound **5-tertbutyl** (200 MHz, $CDCl_3$)

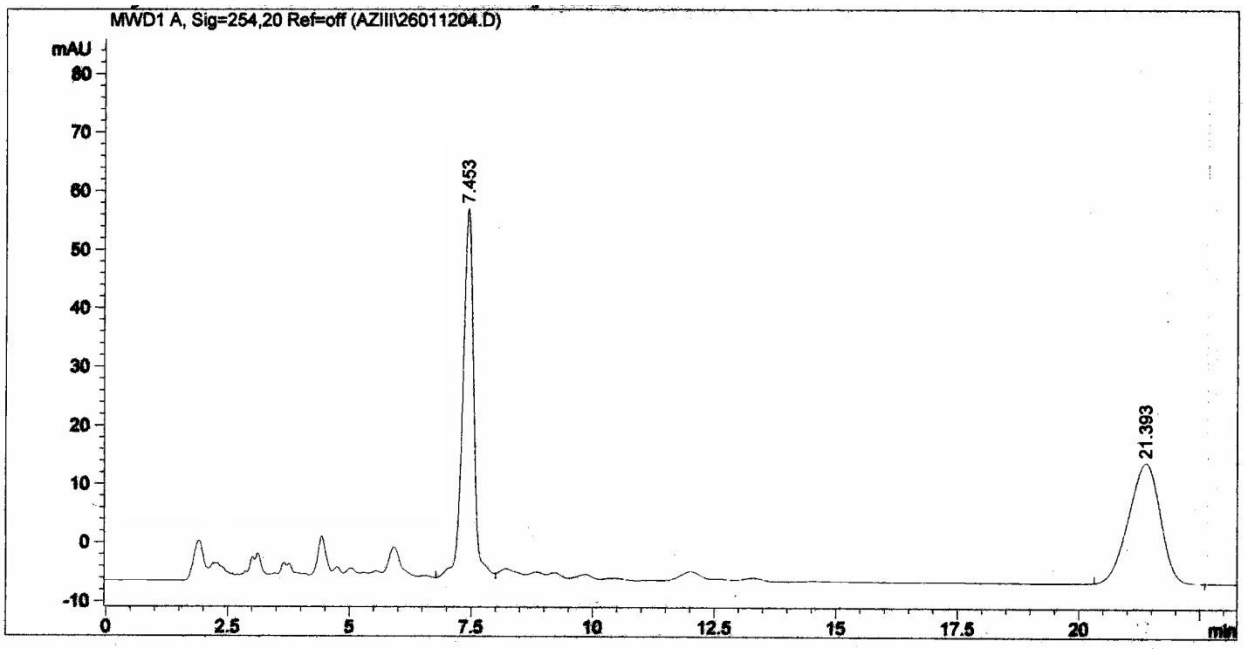


^{1}H NMR Spectrum of compound **5-dibenzyl** (200 MHz, $CDCl_3$)



^{1}H NMR Spectrum of compound **7** (200 MHz, $CDCl_3$)

HPLC Chromatogram



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

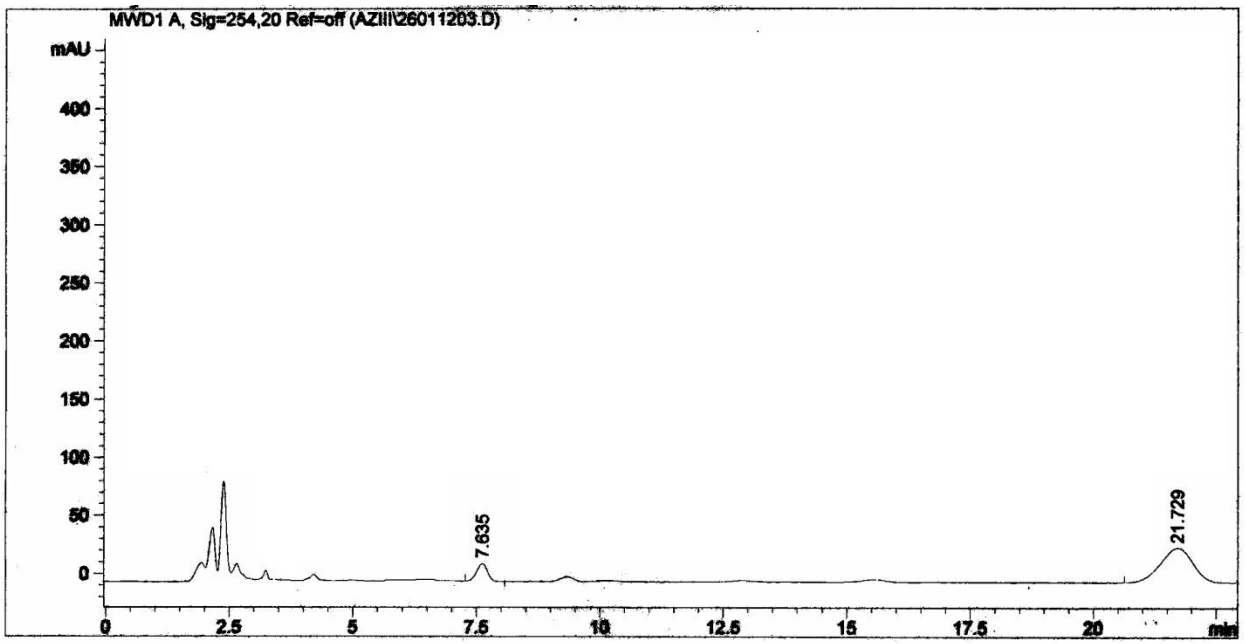
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.453	1	VV	1013.20093	63.25758	51.8367
2	21.393	1	BB	941.40216	20.53154	48.1633
Totals :				1954.60309	83.78911	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6a.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

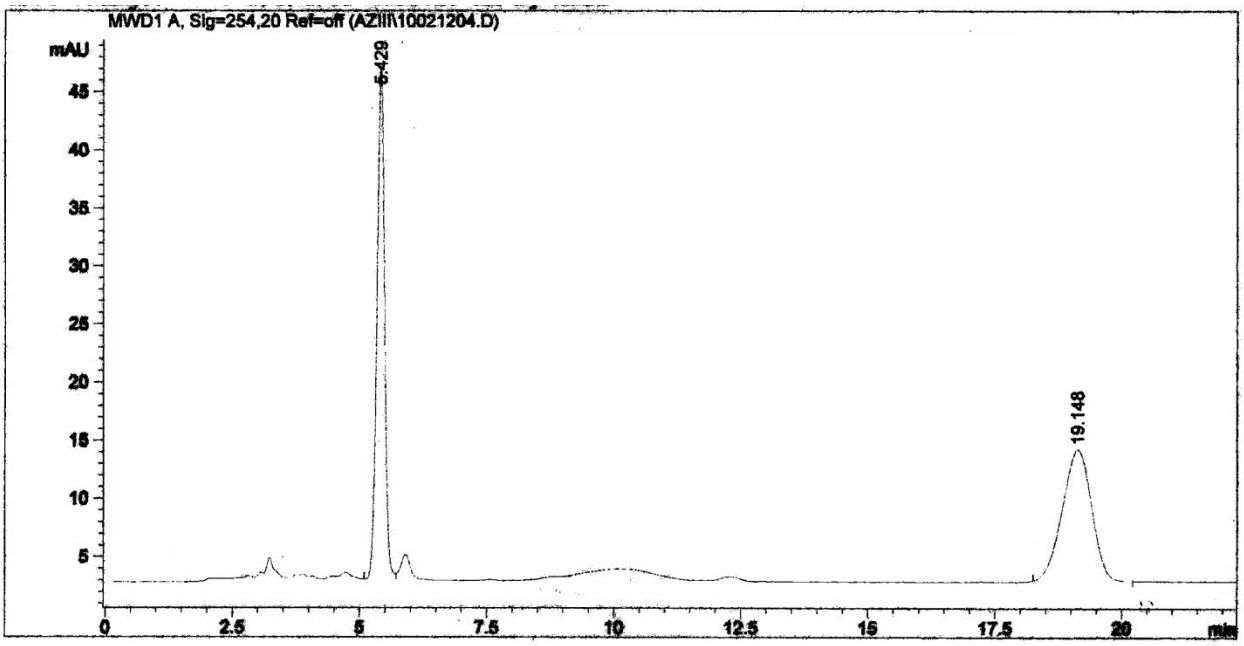
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.635	1	PP	227.89955	15.16945	14.2423
2	21.729	1	BBA	1372.26514	29.54702	85.7577
Totals :				1600.16469	44.71647	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6a.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

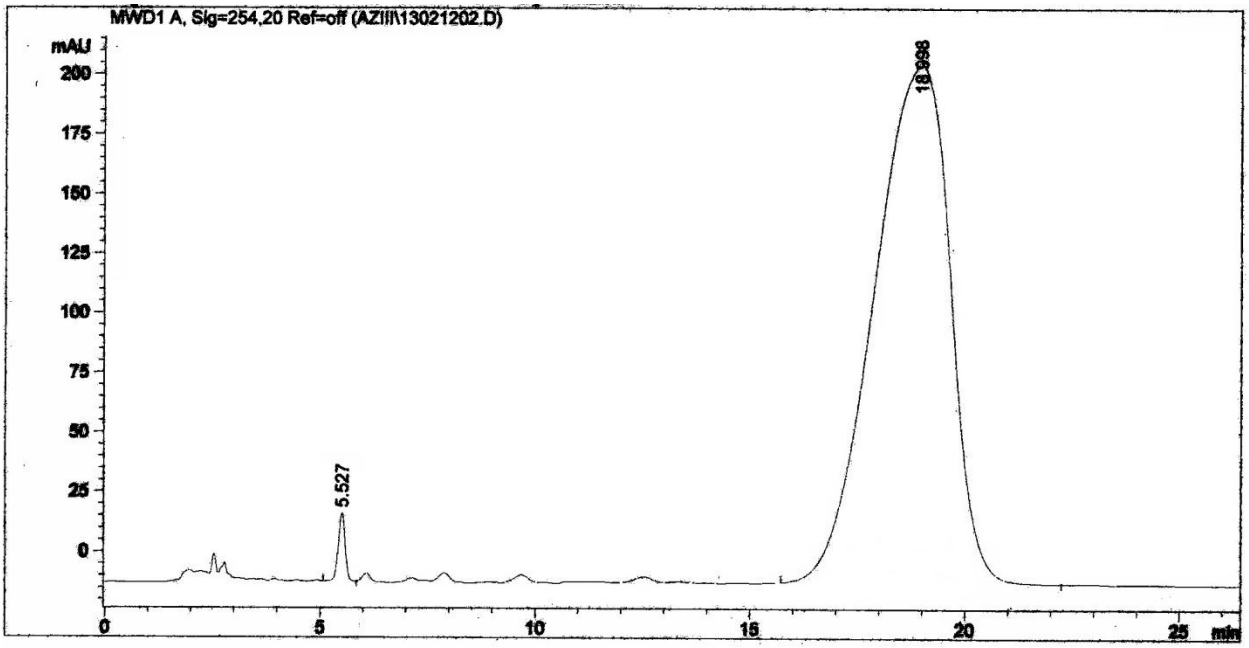
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	5.429	1	VV	466.24744	44.18276	50.3512
2	19.148	1	BB	459.74316	11.33720	49.6488
Totals :				925.99060	55.51997	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6b.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

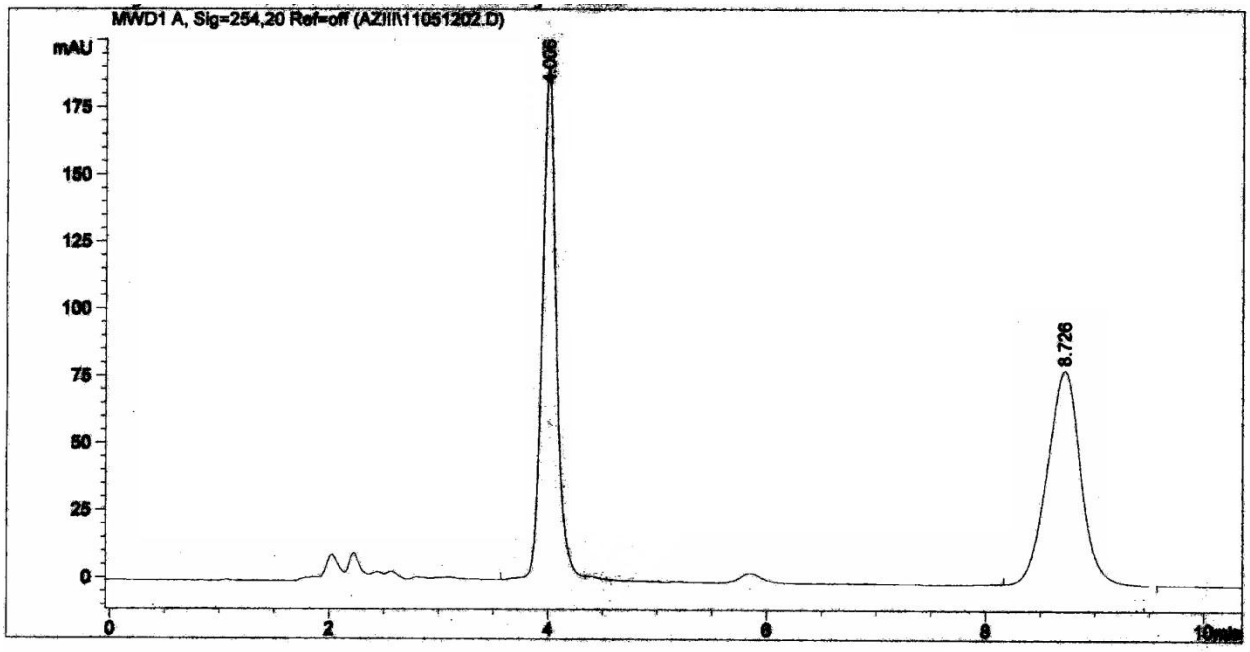
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	5.527	1	VV	336.21027	28.86127	1.2506
2	18.998	1	BB	2.65487e4	216.98715	98.7494
Totals :				2.68849e4	245.84842	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6b.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

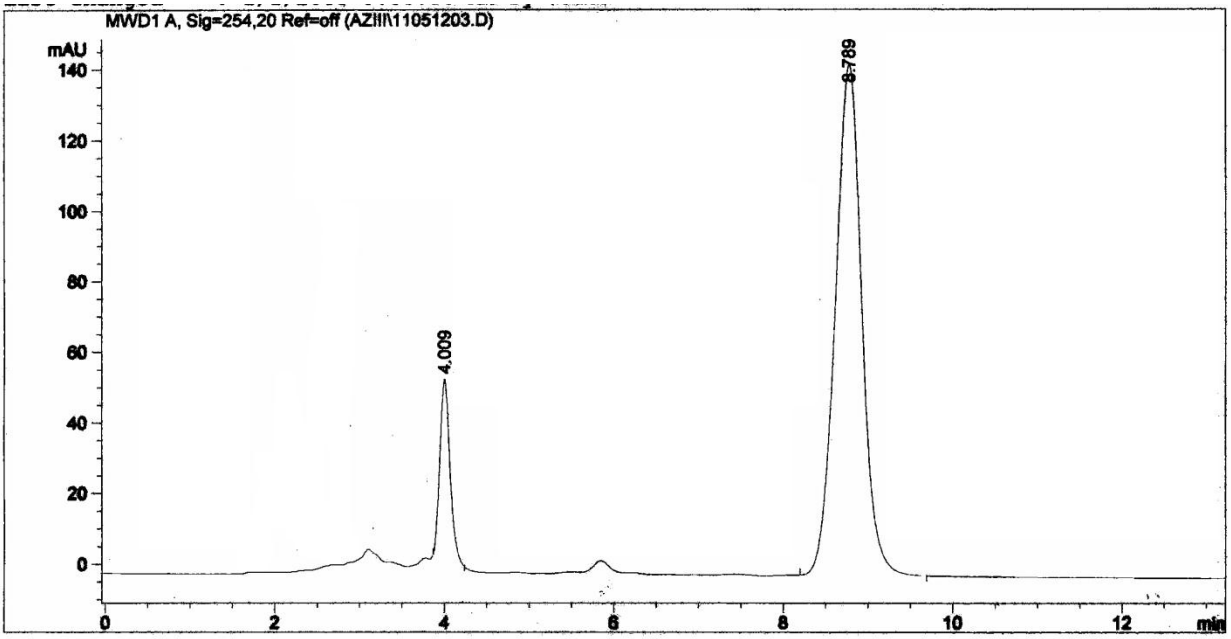
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	4.006	1	VV	1739.36560	191.74780	50.5753
2	8.726	1	BP	1699.79126	79.53378	49.4247
Totals :				3439.15686	271.28159	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6c.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

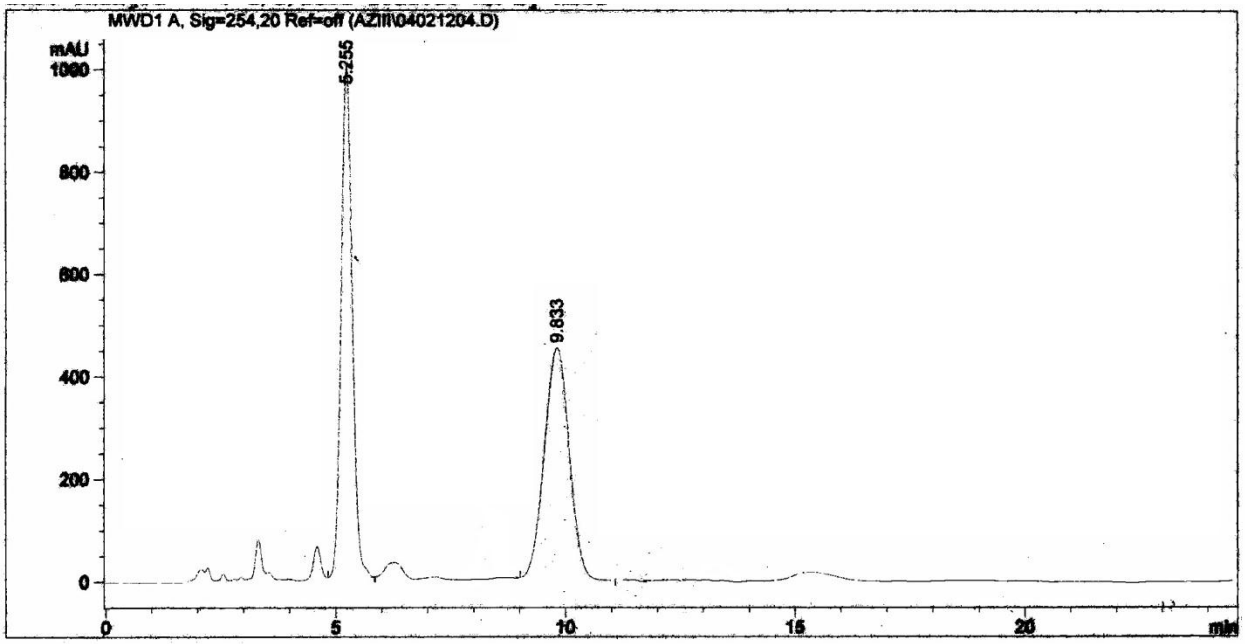
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	4.009	1	MM T	432.38156	51.52673	12.0959
2	8.789	1	BB	3142.21899	144.38614	87.9041
Totals :				3574.60056	195.91287	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6c.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

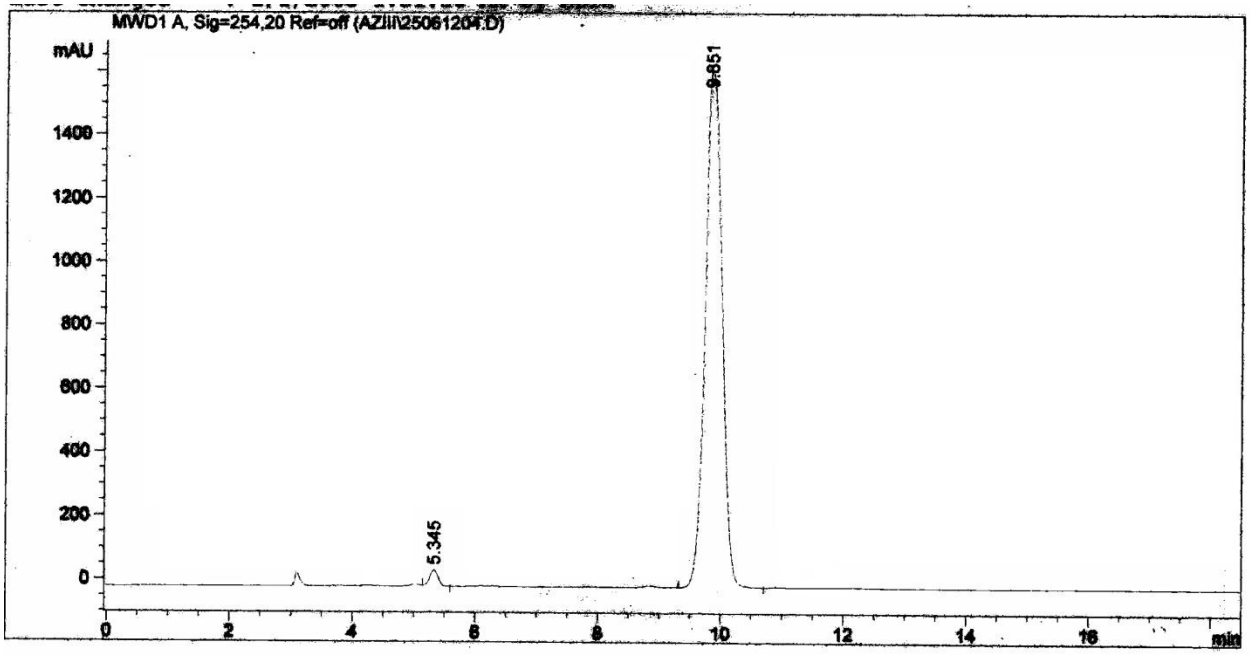
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	5.255	1	VV	1.74754e4	1008.01404	49.8463
2	9.833	1	VB	1.75832e4	456.94421	50.1537
Totals :				3.50586e4	1464.95825	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6d.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

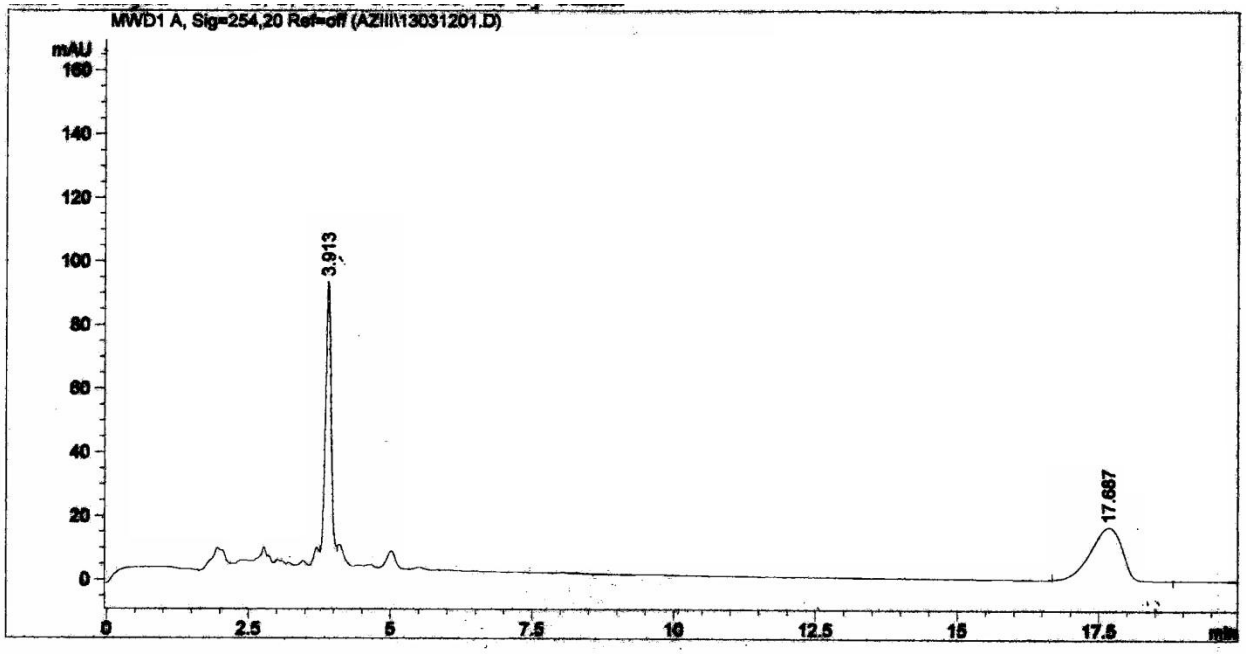
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	5.345	1	VV	535.04926	52.65610	1.6907
2	9.851	1	VV	3.11121e4	1629.88794	98.3093
Totals :				3.16472e4	1682.54404	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6d.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

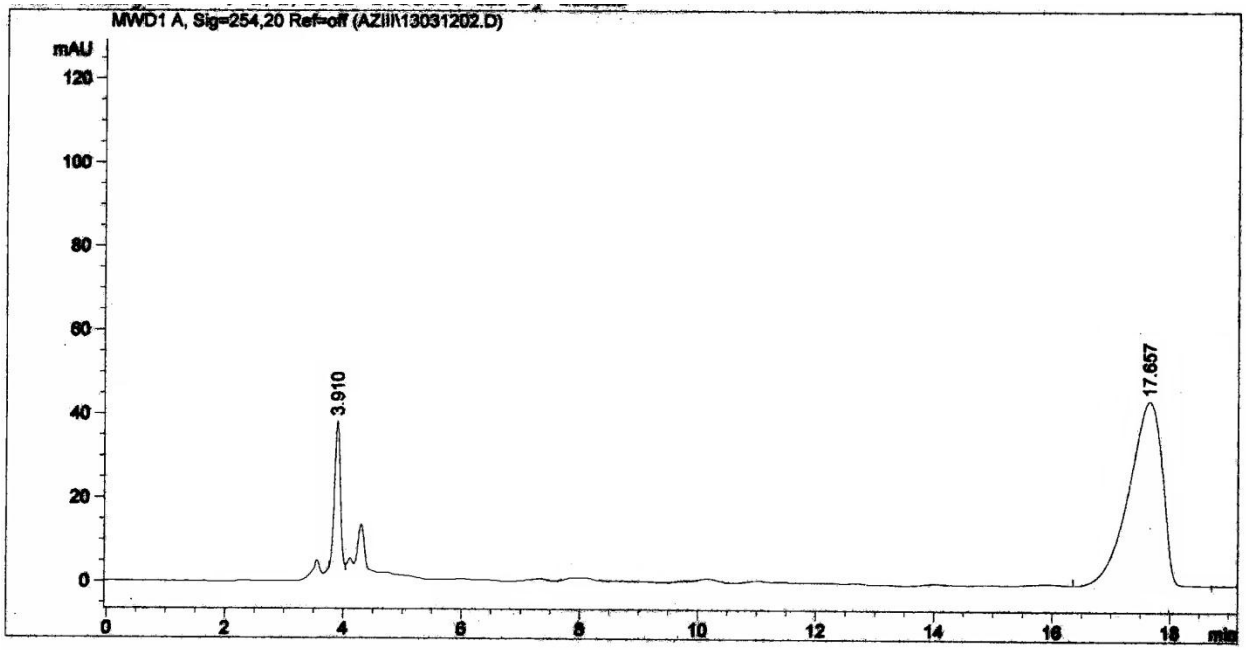
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	3.913	1	VV	702.14691	92.23205	51.9019
2	17.687	1	BP	650.68677	16.68820	48.0981
Totals :				1352.83368	108.92024	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6e.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

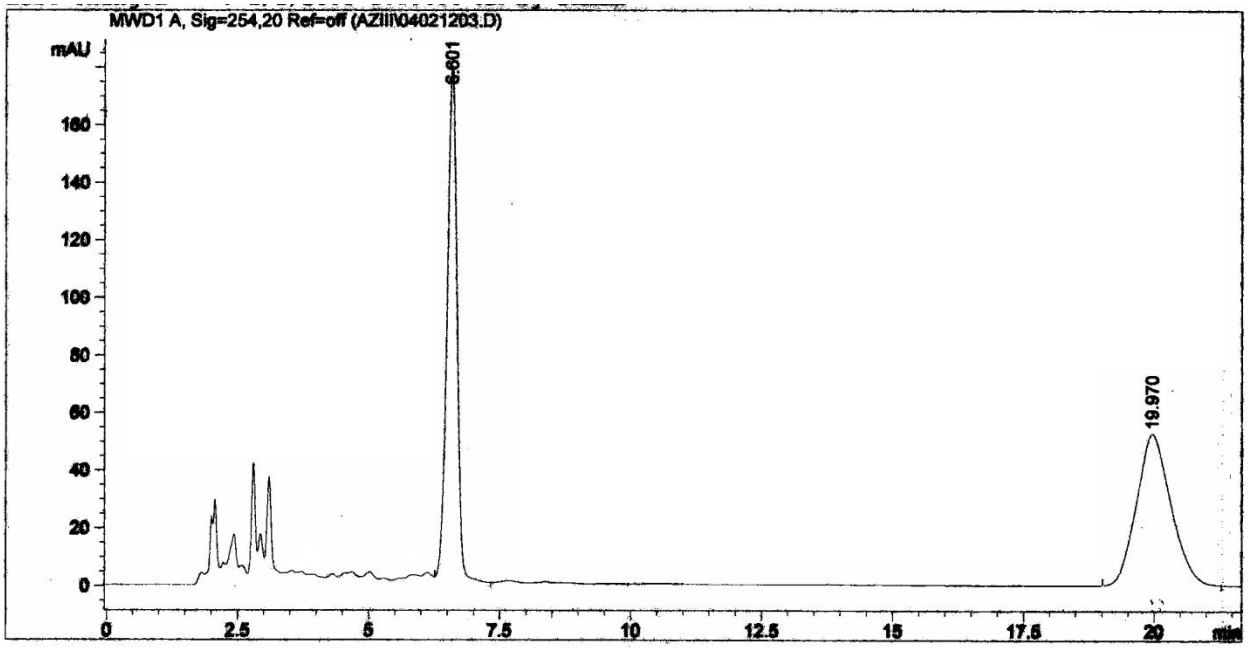
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	3.910	1	MM T	238.37000	35.02024	12.1046
2	17.657	1	VB	1730.88782	43.87981	87.8954
Totals :				1969.25781	78.90006	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6e.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

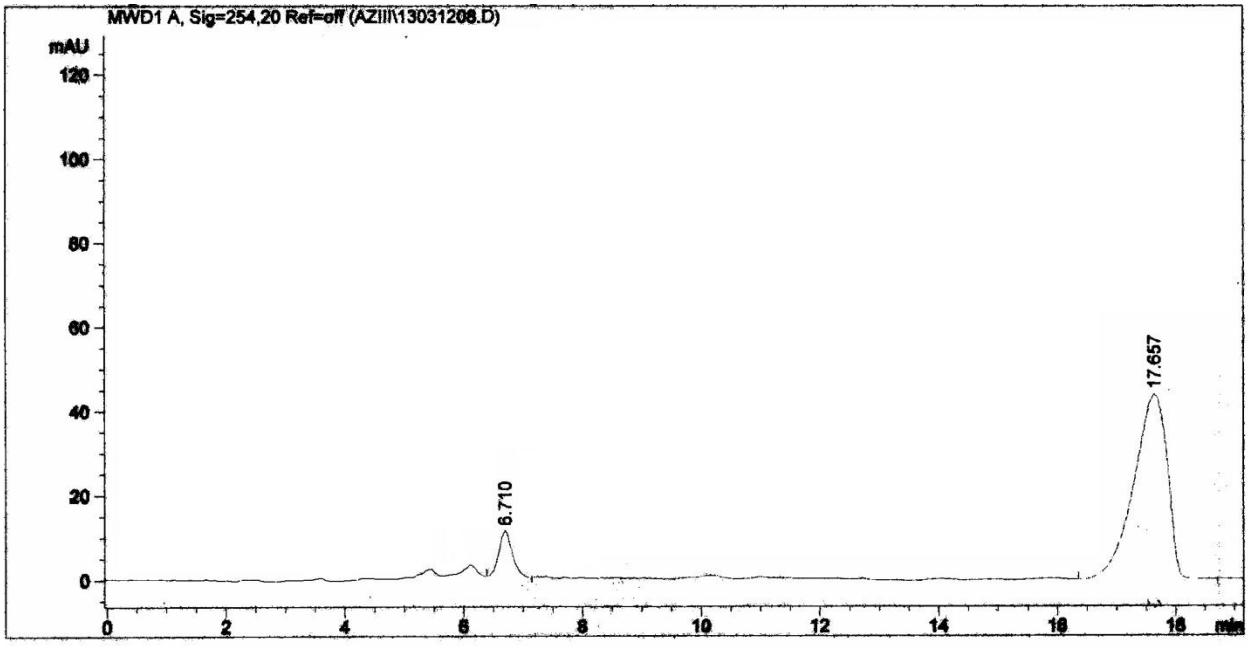
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	6.601	1	VB	2447.01343	179.85165	50.3484
2	19.970	1	BB	2413.15161	52.52795	49.6516
Totals :				4860.16504	232.37960	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6f.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

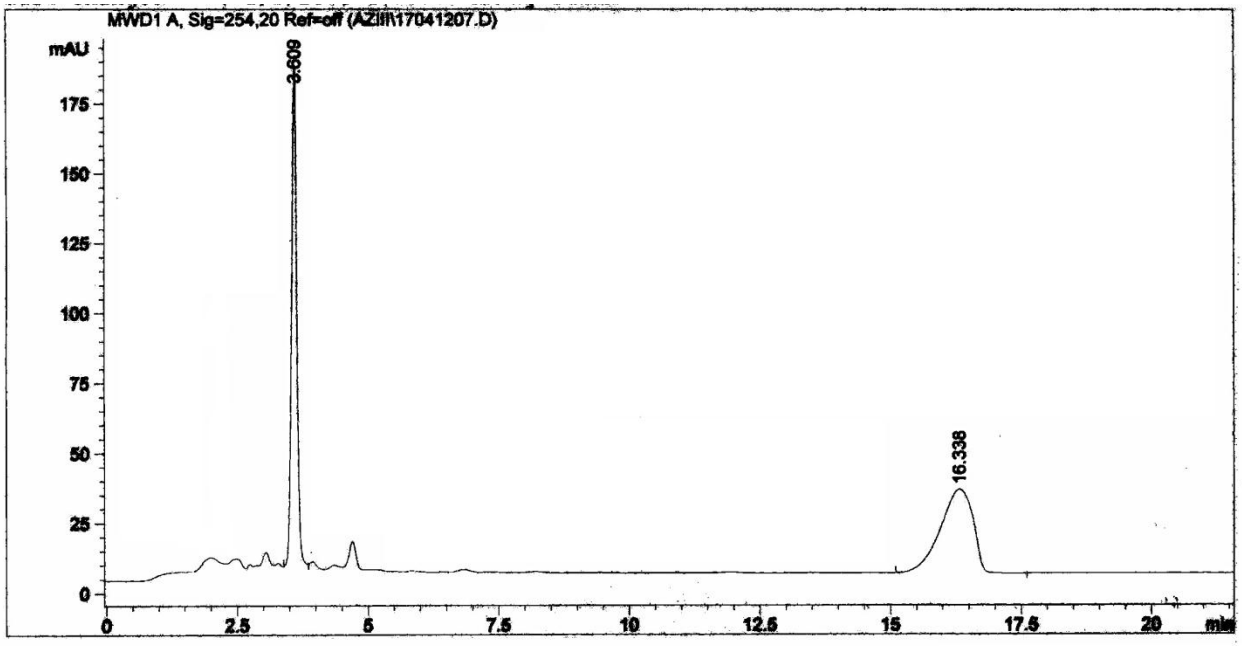
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	6.710	1	VV	189.16489	11.38912	9.8521
2	17.657	1	VB	1730.88782	43.87981	90.1479
Totals :				1920.05270	55.26893	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6f.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

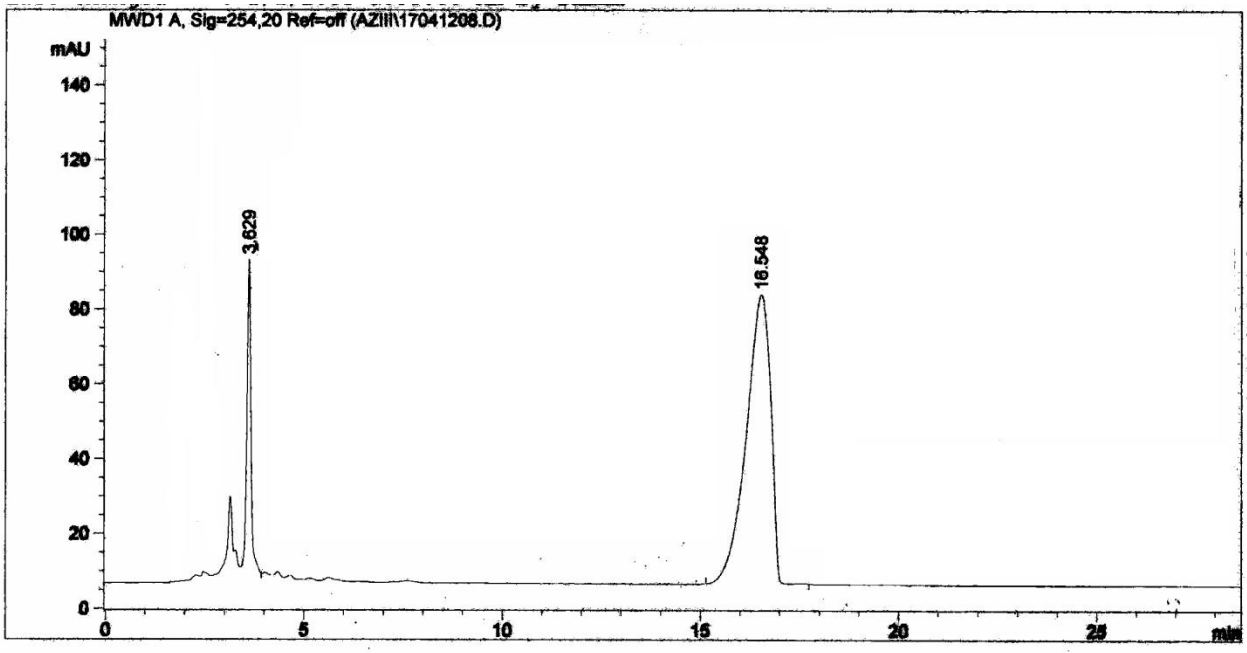
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	3.609	1	VV	1337.30457	181.77211	50.7274
2	16.338	1	BP	1298.95056	29.92642	49.2726
Totals :				2636.25513	211.69853	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6g.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

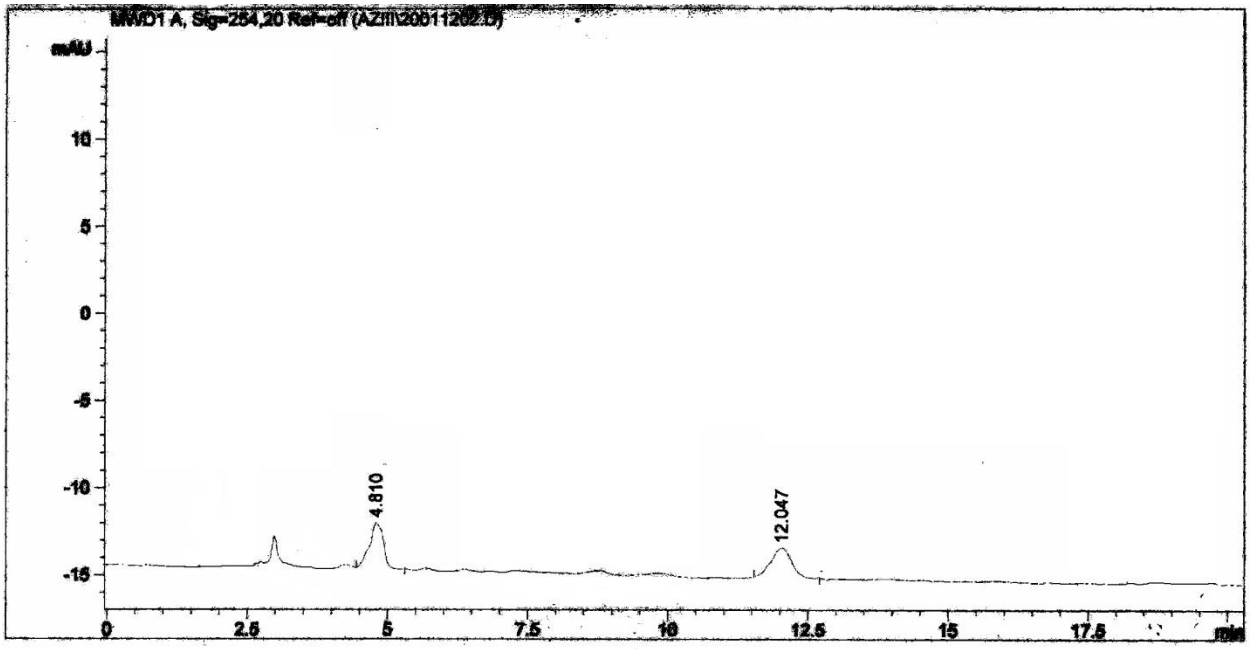
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	3.629	1	MM T	587.08673	82.46165	14.9667
2	16.548	1	BB	3335.52393	77.39643	85.0333
Totals :				3922.61066	159.85809	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6g.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

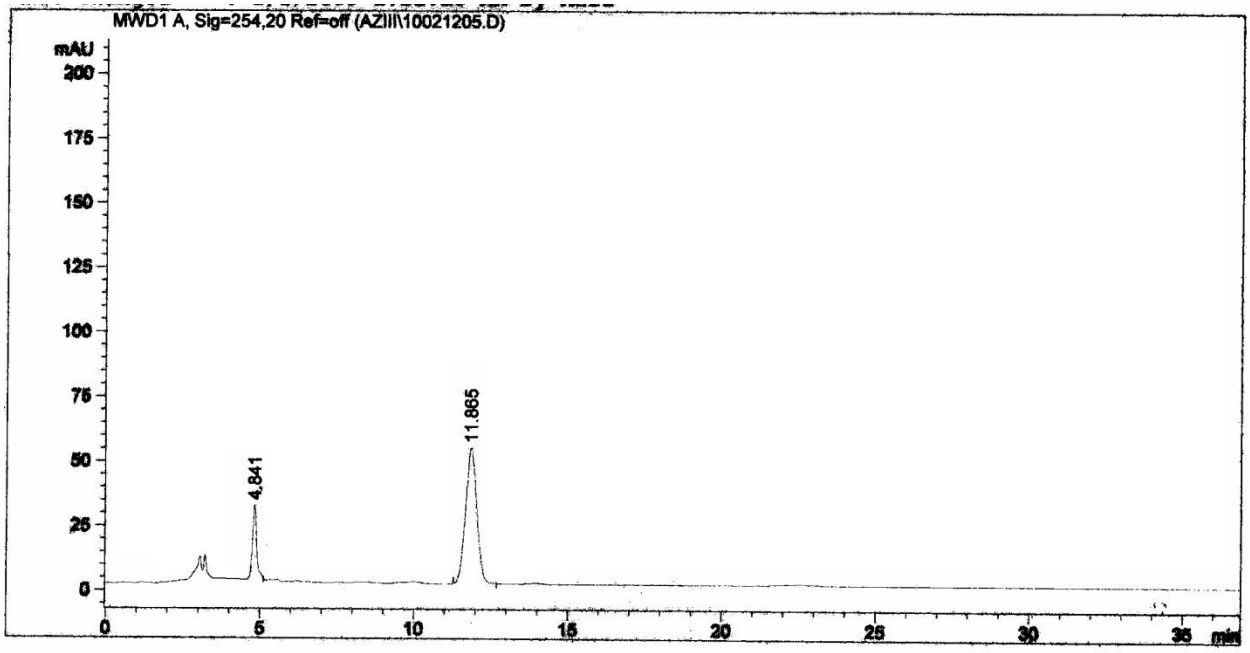
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	4.810	1	VB	47.06750	2.67488	51.7353
2	12.047	1	BB	43.90998	1.70030	48.2647
Totals :				90.97748	4.37518	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6h.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

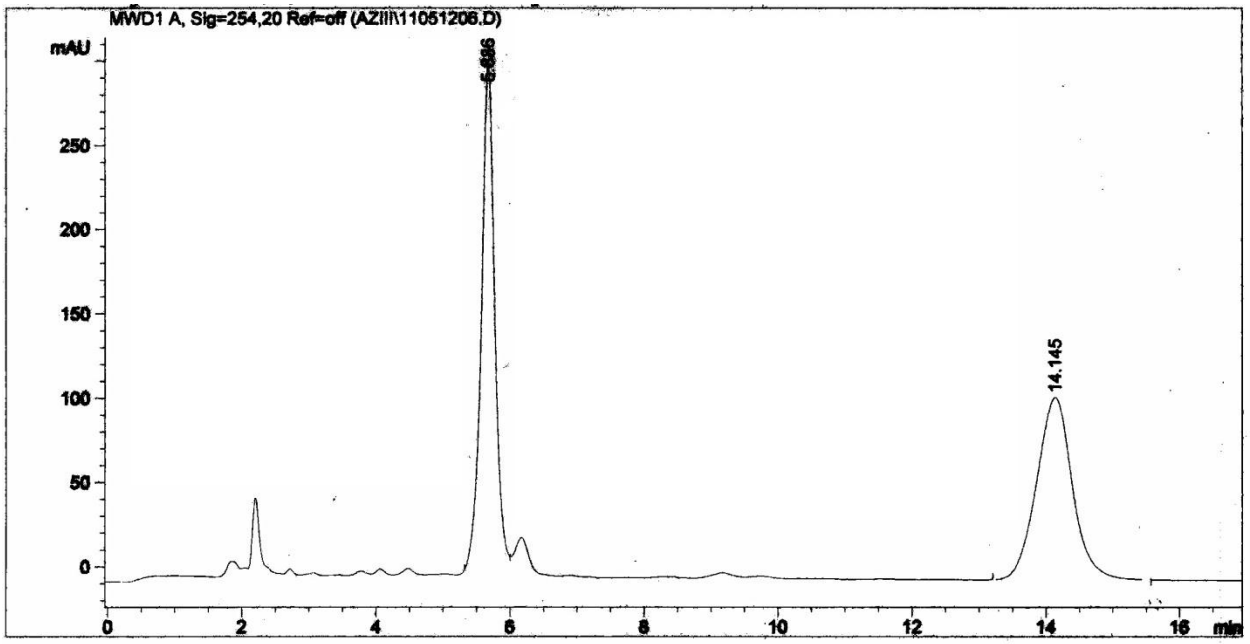
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	4.841	1	MP	252.62100	27.92311	15.8253
2	11.865	1	BB	1343.69055	52.60855	84.1747
Totals :				1596.31155	80.53166	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6h.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

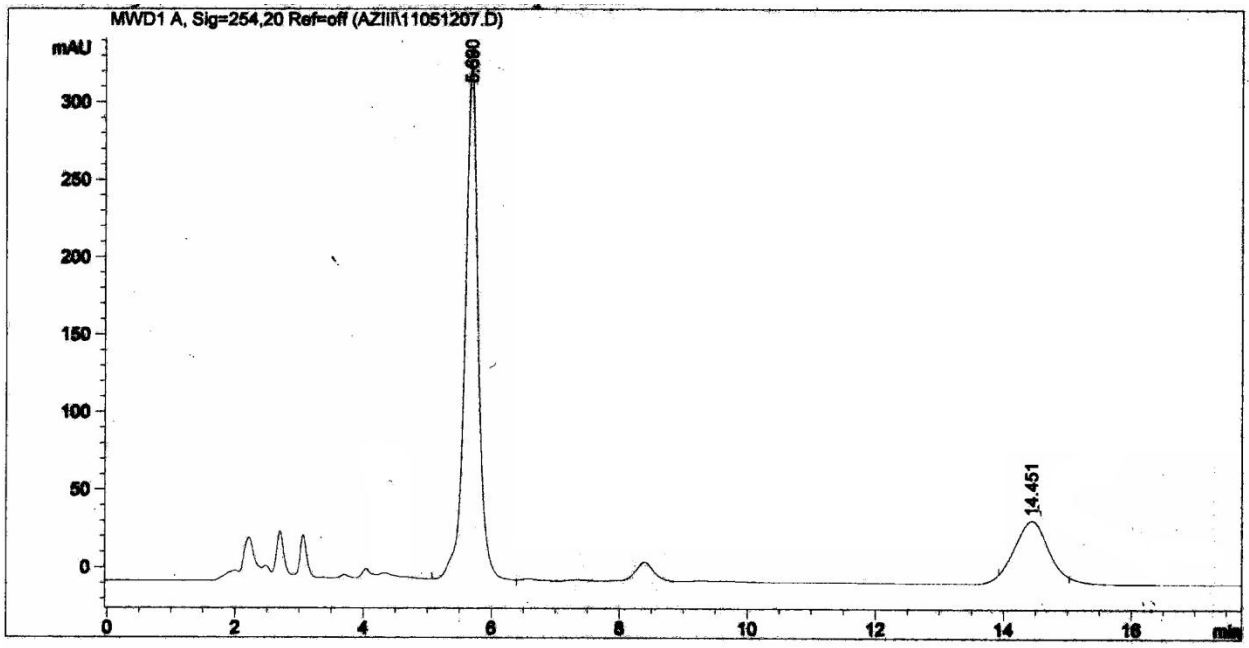
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	5.686	1	MM T	4083.19214	297.25876	50.3382
2	14.145	1	BB	4028.32983	108.12383	49.6618
Totals :				8111.52197	405.38258	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6i.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

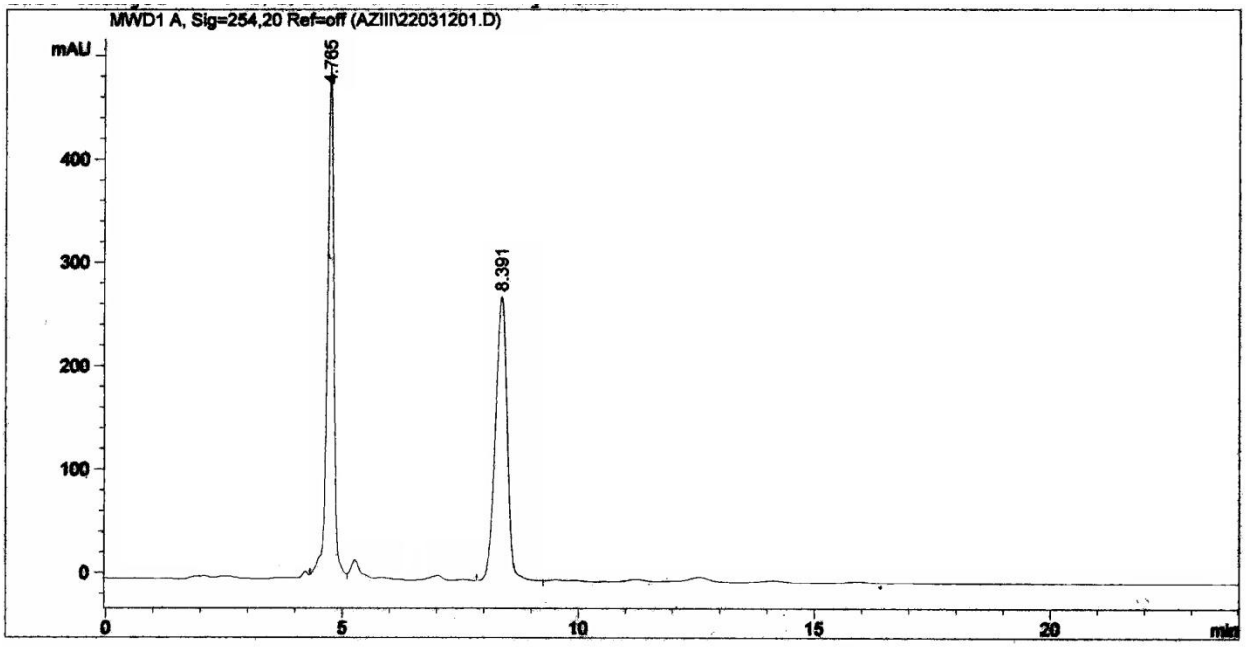
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	5.690	1	VB	4871.84375	332.93845	79.5567
2	14.451	1	MM T	1251.89307	36.88488	20.4433
Totals :				6123.73682	369.82332	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6i.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

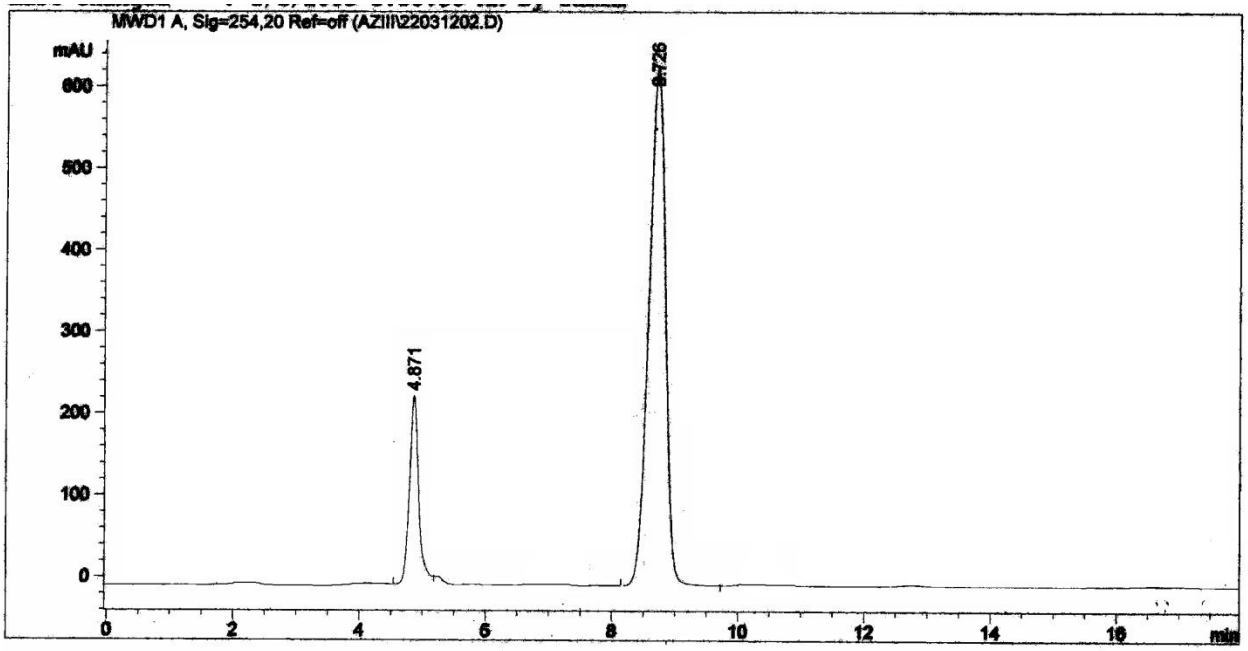
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	4.765	1	VV	4970.08057	497.74753	50.7287
2	8.391	1	VV	4827.28906	274.52292	49.2713
Totals :				9797.36963	772.27045	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6j.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

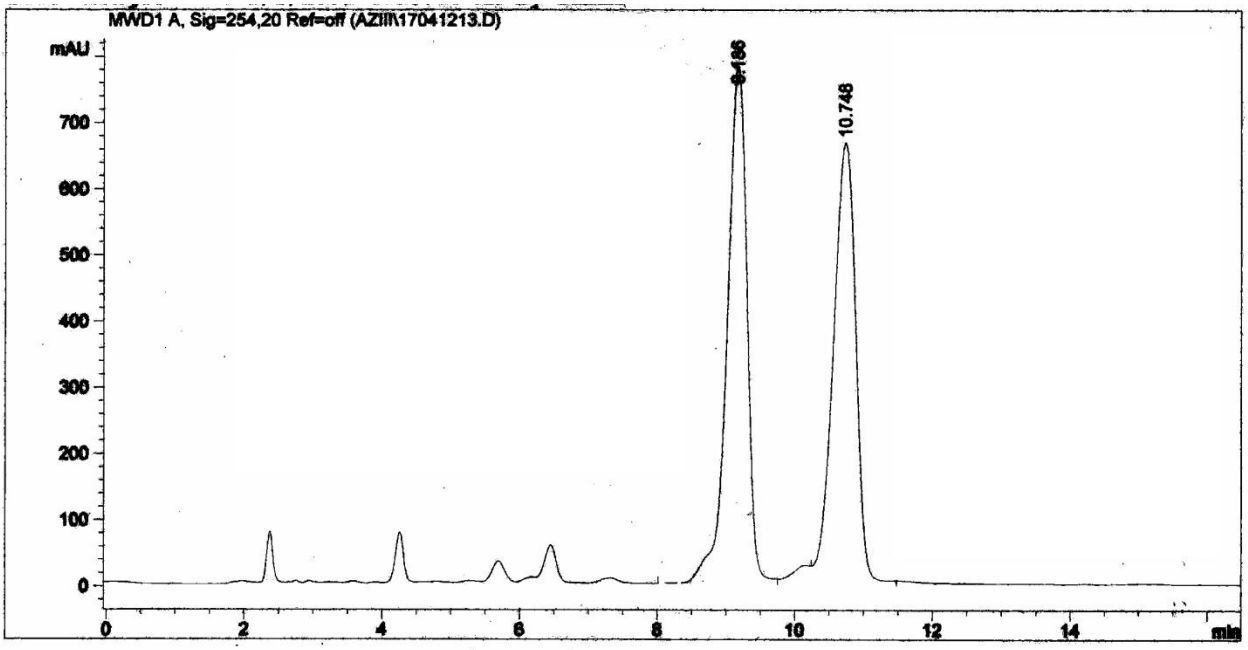
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	4.871	1	VV	2418.84546	231.35249	17.1161
2	8.726	1	BB	1.17131e4	632.45837	82.8839
Totals :				1.41320e4	863.81087	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6j.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

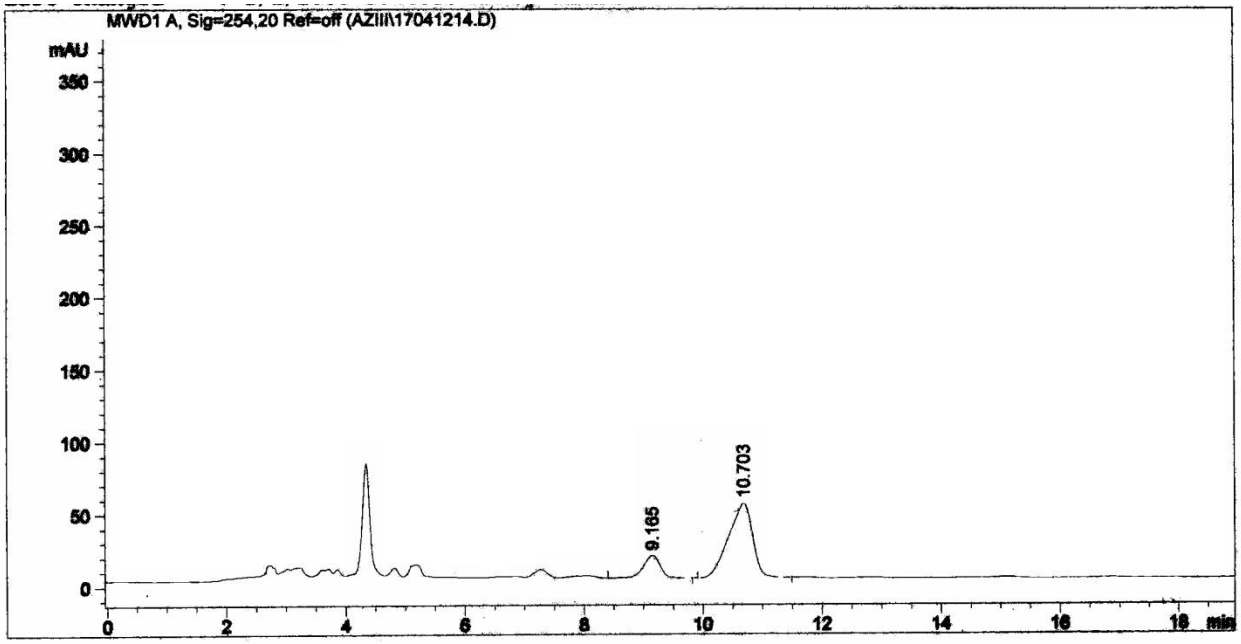
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.186	1	PV	1.57207e4	781.07617	50.9648
2	10.748	1	VB	1.51254e4	664.83374	49.0352
Totals :				3.08461e4	1445.90991	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6k.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

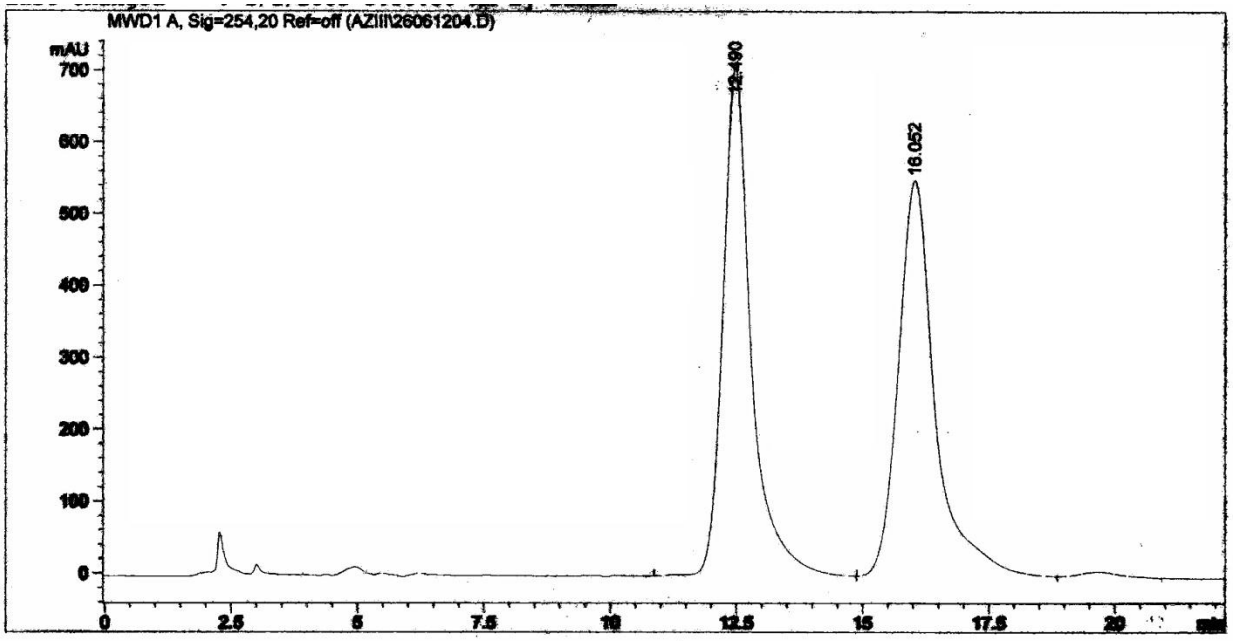
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.165	1	VP	329.19025	16.01503	18.5549
2	10.703	1	BP	1444.95483	51.75391	81.4451
Totals :				1774.14508	67.76893	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6k.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

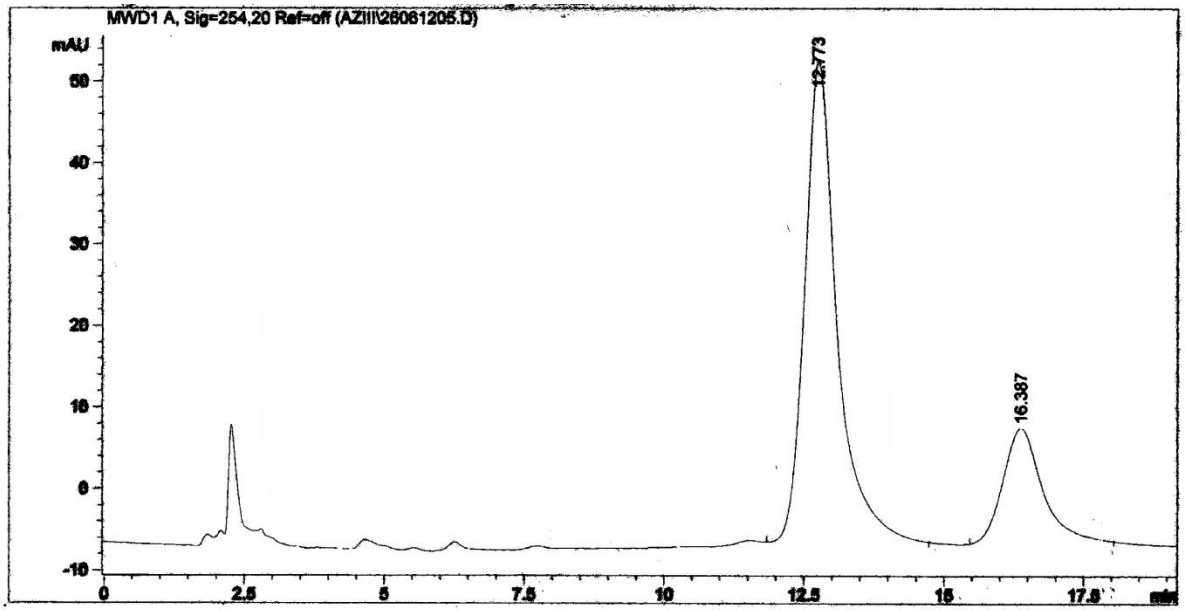
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	12.490	1	BB	2.79555e4	709.48303	49.7242
2	16.052	1	BB	2.82657e4	552.69781	50.2758
Totals :				5.62212e4	1262.18085	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6l.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

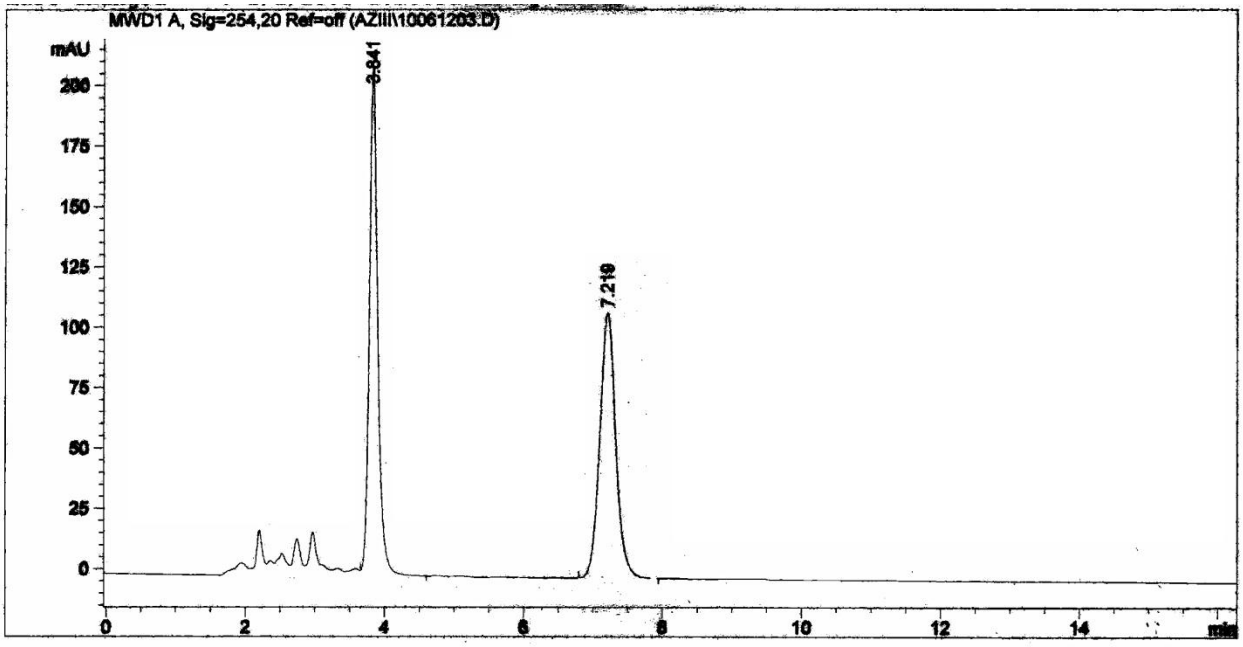
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	12.773	1	VB	2409.20776	59.23946	77.4637
2	16.387	1	BB	700.90509	14.14289	22.5363
Totals :				3110.11285	73.38235	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6l.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

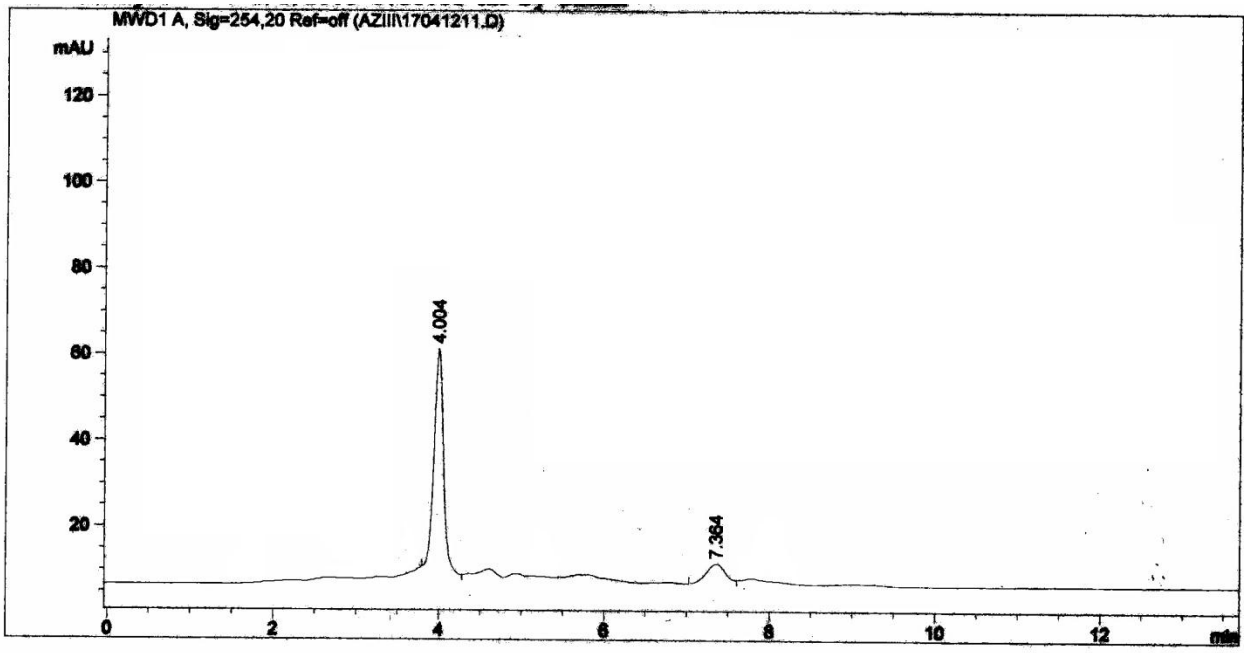
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	3.841	1	VB	1809.27136	211.41501	50.6136
2	7.219	1	BB	1765.40381	109.74596	49.3864
Totals :				3574.67517	321.16096	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6-isopropyl.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

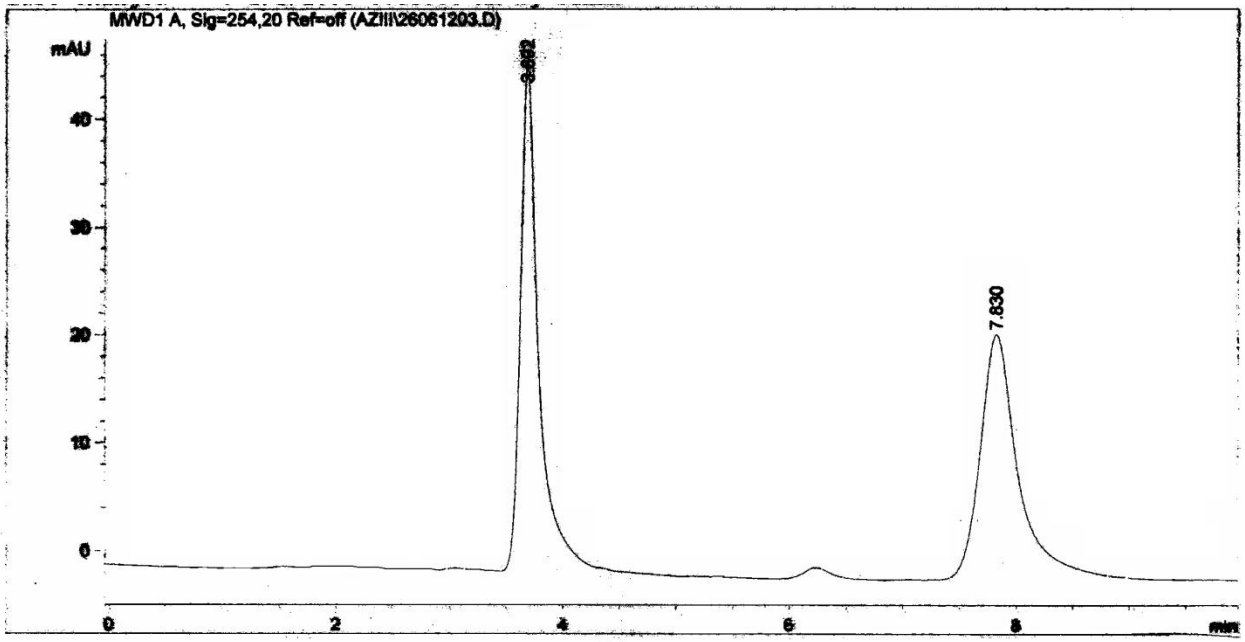
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	4.004	1	VV	493.96329	54.54877	86.7729
2	7.364	1	PV	75.29671	4.64000	13.2271
Totals :				569.25999	59.18877	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6-isopropyl.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

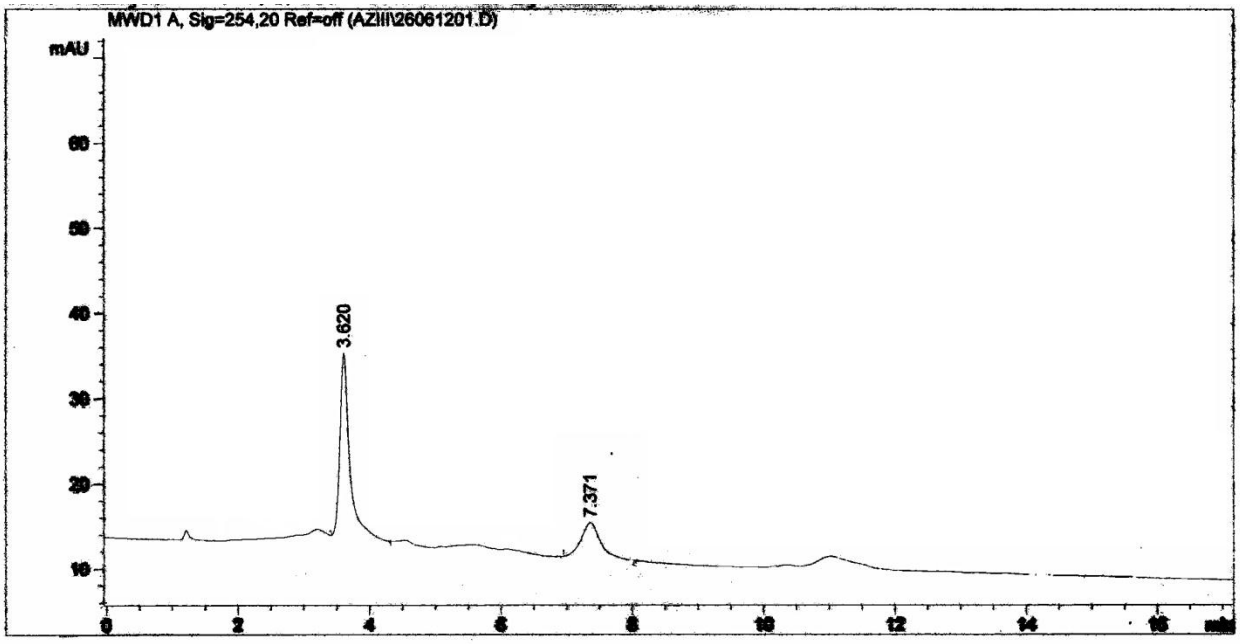
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	3.692	1	VB	547.31183	47.26089	50.8258
2	7.830	1	BB	529.52716	22.64694	49.1742
Totals :				1076.83899	69.90783	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6-tertbutyl.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 A, Sig=254,20 Ref=off

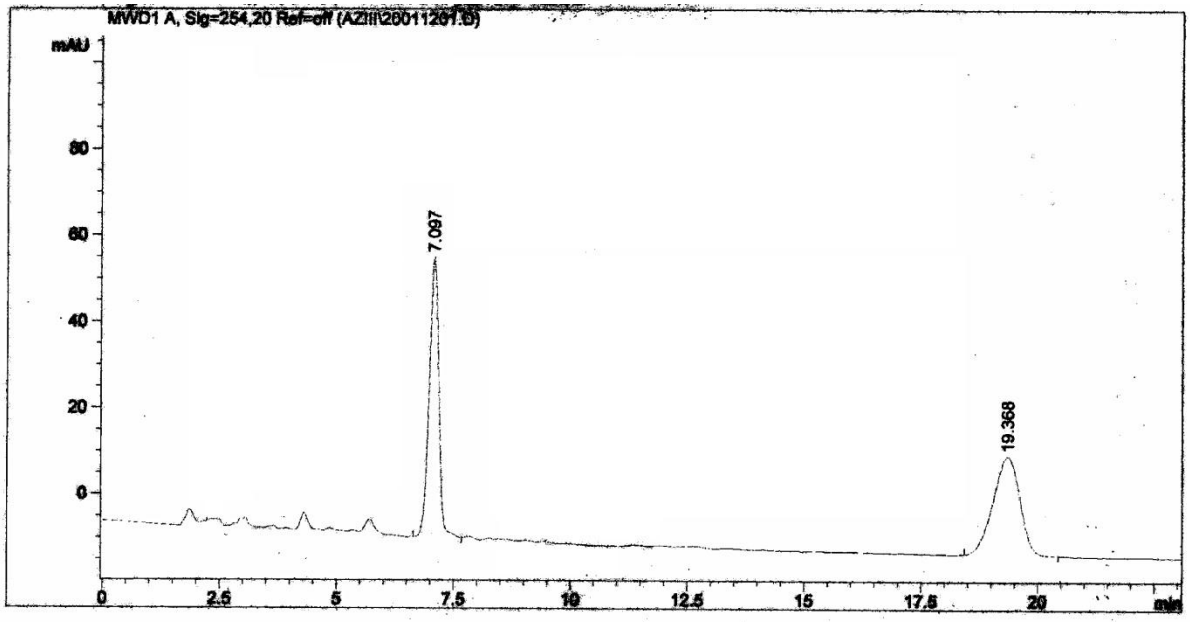
Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	3.620	1	VB	270.19919	22.50666	75.4076
2	7.371	1	BB	88.11923	4.20562	24.5924

Totals : 358.31842 26.71227

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6-tertbutyl.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

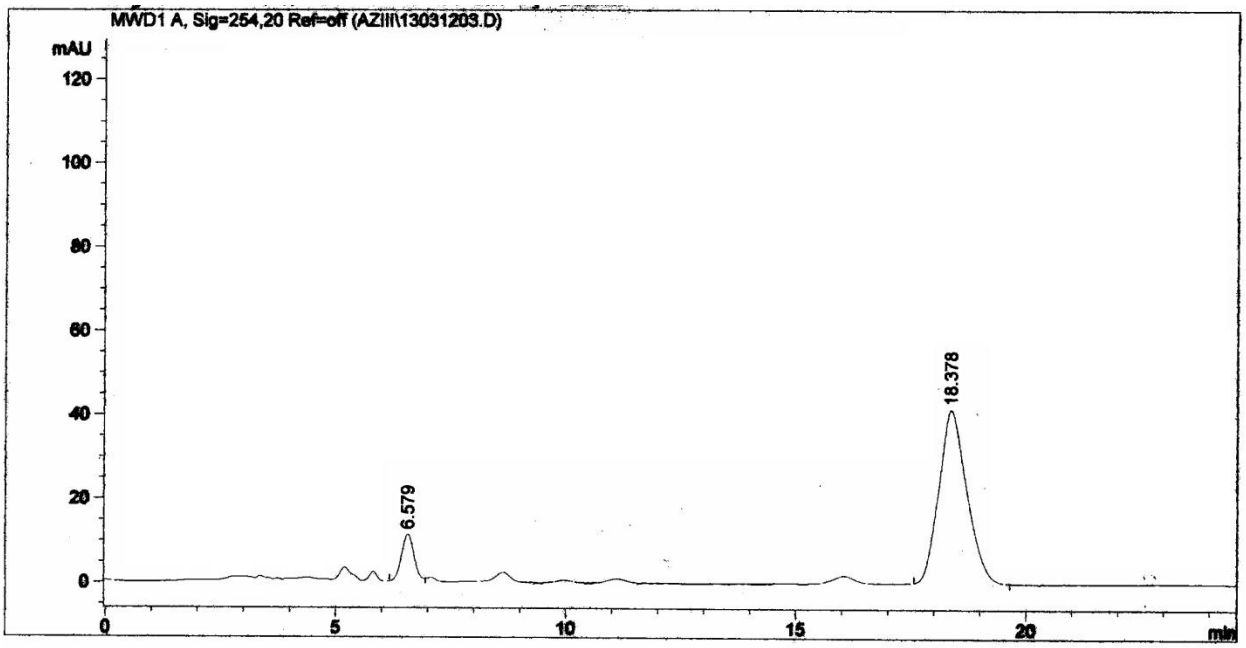
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	7.097	1	PV	944.42462	65.07190	50.6449
2	19.368	1	BB	920.37402	22.85592	49.3551
Totals :				1864.79865	87.92782	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 6-dibenzyl.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

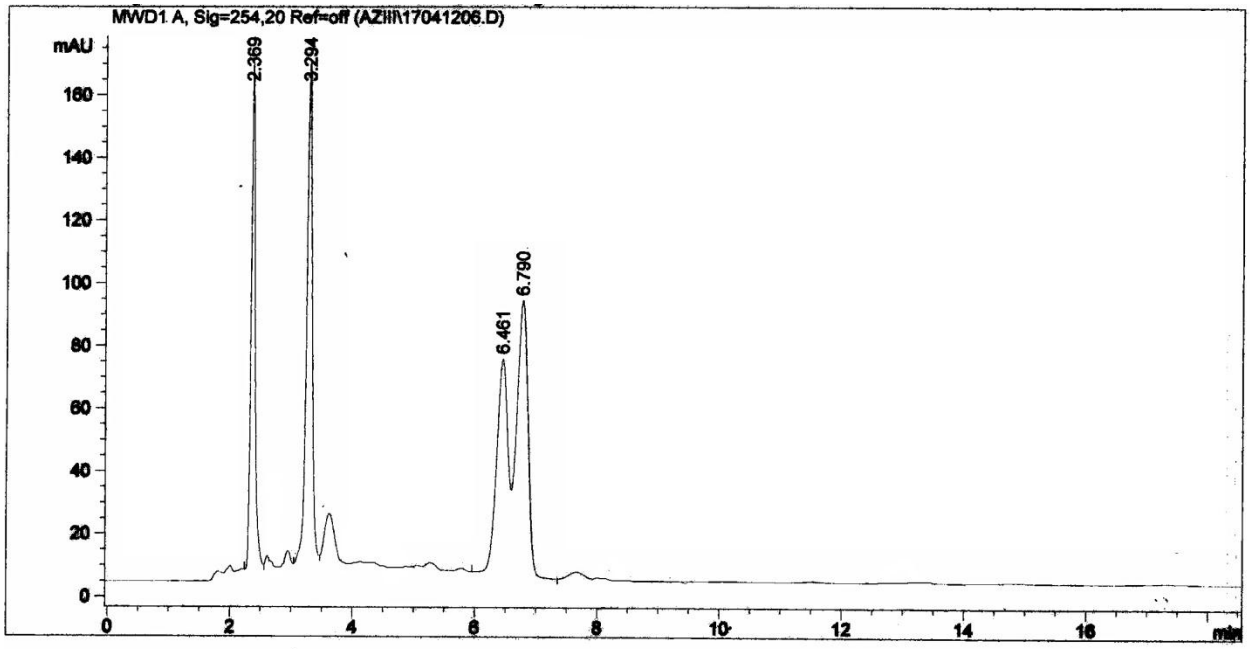
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	6.579	1	BV	215.33363	11.21601	10.9129
2	18.378	1	BB	1757.86255	41.30775	89.0871
Totals :				1973.19618	52.52376	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **6-dibenzyl.**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

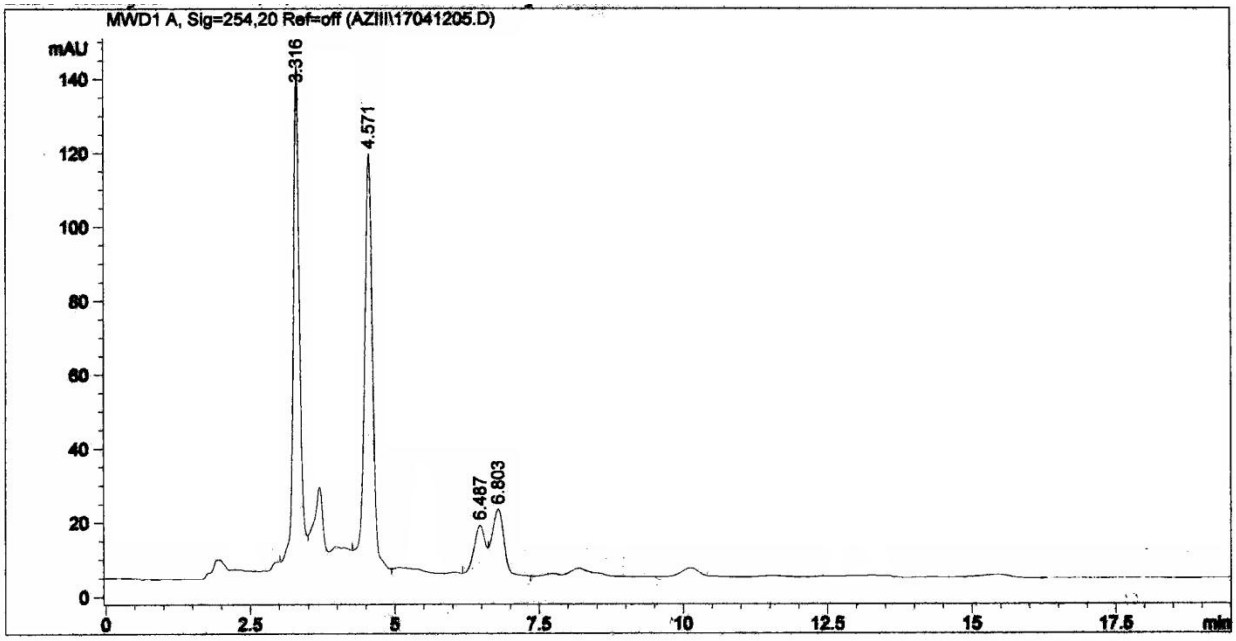
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	2.369	1	VV	839.66534	165.72096	20.0111
2	3.294	1	VV	1176.10364	165.63101	28.0292
3	6.461	1	VV	976.36072	70.80771	23.2689
4	6.790	1	VB	1203.86841	89.50025	28.6909
Totals :				4195.99811	491.65993	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **(±) 8**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	3.316	1	VV	1137.23425	139.20958	40.3531
2	4.571	1	VV	1204.91431	114.77251	42.7546
3	6.487	1	VV	199.23903	14.06383	7.0697
4	6.803	1	VB	276.82022	18.35784	9.8226
Totals :				2818.20781	286.40375	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **8.**