Supporting Information

Organocatalytic Synthesis of *N*-Phenylisoxazolidin-5-ones and a One-Pot Synthesis of β-Amino Acid Esters

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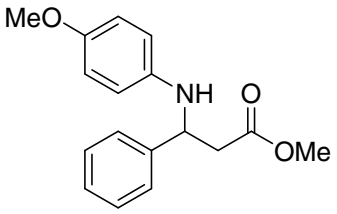
General: Reactions were monitored by thin layer chromatography using 0.25-mm E. Merck silica gel coated glass plates (60F-254) with UV light to visualize the course of reaction. Flash column chromatography was performed using CombiFlash (ISCO, Inc.). Chemical yields referred to the pure isolated substances. Gas chromatography-mass spectrometry (GC-MS) was performed with Shimadzu GC-2010 coupled with GCMS-QP2010. ^{1}H and ^{13}C NMR spectra were obtained using a Brucker AV-400 (400 MHz) spectrometer. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. Data were reported in the following order: chemical shift in ppm (δ) (multiplicity were indicated by br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), m_c (centered multiplet)); coupling constants (*J*, Hz); integration; assignment. All reactions were performed in oven-dried (140°C) or flame-dried glassware under an inert atmosphere of dry N_2 or Ar. All solvents were anhydrous and purchased from Aldrich or Fluka.

Procedure for the NHC-catalyzed synthesis of β-aminoesters: KO^tBu (0.2 mmol) was added under Ar to a solution of α,β-unsaturated aldehyde (1 mmol), nitrosobenzene (1.1 mmol) and the catalyst (0.1–0.2 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 1–6 h. The solvent was removed under vacuum, and the residue was diluted with methanol (3 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.

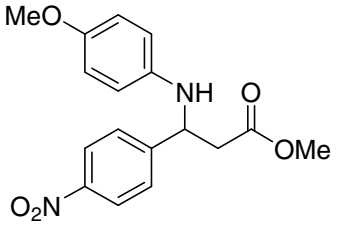
Methyl 3-(4-methoxyphenylamino)-3-phenylpropanoate (9a): Potassium *tert*-butoxide (22.4 mg, 0.2 mmol) was added to a solution of (*E*)-cinnamaldehyde (132 mg, 1 mmol), nitrosobenzene (117 mg, 1.1 mmol) and the catalyst (85 mg, 0.2 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed under vacuum, and the residue was diluted with methanol (3 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.25 (m, 5H, Ar-H), 6.71 (AB, d, J_{AB} = 8.4 Hz, 2H, Ar-H), 6.56 (AB, d, J_{AB} = 8.4 Hz, 2H, Ar-H), 4.77 (t, J = 6.4 Hz, 1H, CH), 4.32 (br s, 1H, NH), 3.71 (s, 3H, CH_3), 3.66 (s, 3H, CH_3), 2.84 (d, J = 6.4 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7 (Cq, CO), 152.6, 142.0, 140.3 (Cq), 128.8, 127.5, 126.4 (C-Ar), 115.6, 114.7 (C-Ar), 56.2, 55.7 (OCH_3), 51.9 (CH), 42.5 (CH_2). MS (ESI): *m/z* 285 (M^+), 212, 122.

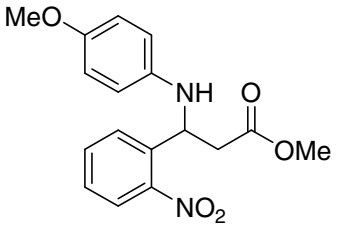
Methyl 3-(4-methoxyphenylamino)-3-(4-nitrophenyl)propanoate (9b): Potassium *tert*-butoxide (11.2 mg, 0.1 mmol) was added to a solution of (*E*)-4-nitrocinnamaldehyde (177 mg, 1 mmol), nitrosobenzene (117 mg, 1.1 mmol) and the catalyst (42.5 mg, 0.1 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 3 h. The solvent was removed under vacuum, and the residue was diluted with methanol (3 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then by brine (10 mL), dried ($MgSO_4$), and concentrated. The pure

product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (AB, d, J_{AB} = 8.6 Hz, 2H, Ar-H), 7.57 (AB, d, J_{AB} = 8.6 Hz, 2H, Ar-H), 6.70 (AB, d, J_{AB} = 8.8 Hz, 2H, Ar-H), 6.48 (AB, d, J_{AB} = 8.8 Hz, 2H, Ar-H), 4.87 (br t, J = 6.6 Hz, 1H, CH), 4.30 (br s, 1H, NH), 3.70 (s, 3H, CH_3), 3.67 (s, 3H, CH_3), 2.83 (dd, J = 2.0, 6.6 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1 (Cq, CO), 152.7, 150.2, 147.3, 140.1 (Cq), 127.4, 124.1 (C-Ar), 115.2, 114.8 (C-Ar), 55.6, 55.3 (OCH_3), 52.1 (CH), 42.1 (CH_2). MS (ESI): *m/z* 330 (M^+), 257, 211, 122, 108.

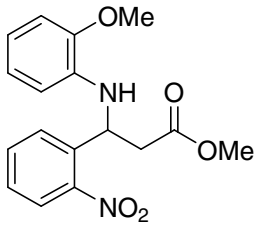
Methyl 3-(4-methoxyphenylamino)-3-(2-nitrophenyl)propanoate (9c): Potassium *tert*-butoxide (22.4 mg, 0.2 mmol) was added to a solution of (*E*)-2-nitrocinnamaldehyde (177 mg, 1 mmol), nitrosobenzene (117 mg, 1.1 mmol) and the catalyst (85 mg, 0.2 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed under vacuum, and the residue was diluted with methanol (3 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (dd, J = 1.2, 8.0 Hz, 1H, Ar-H), 7.73 (dd, J = 1.2, 8.0 Hz, 1H, Ar-H), 7.56 (dt, J = 1.2, 8.0 Hz, 1H, Ar-H), 7.41 (dt, J = 1.2, 8.0 Hz, 1H, Ar-H), 6.68 (AB, d, J_{AB} = 8.8 Hz, 2H, Ar-H), 6.45 (AB, d, J_{AB} = 8.8 Hz, 2H, Ar-H), 5.40 (dd, J = 4.3, 7.9 Hz, 1H, CH), 4.30 (br s, 1H, NH), 3.69 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.04 (dd, J =

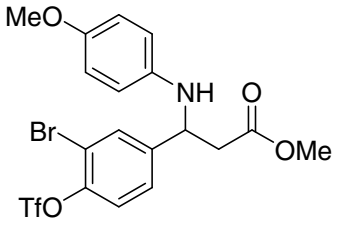
4.3, 15.3 Hz, 1H, CH_2), 2.81 (dd, J = 7.9, 15.3 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4 (Cq, CO), 152.6, 148.9, 140.0, 137.7 (Cq), 133.6, 128.6, 128.4, 125.0 (C-Ar), 116.4, 114.8 (C-Ar), 55.6, 52.0 (OCH_3), 51.4 (CH), 41.2 (CH_2). MS (ESI): *m/z* 330 (M^+), 296, 257, 237, 122, 108.

Methyl 3-(2-methoxyphenylamino)-3-(2-nitrophenyl)propanoate (9c'):



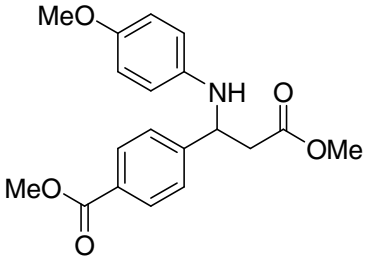
^1H NMR (400 MHz, $CDCl_3$): δ 7.98 (dd, J = 1.1, 8.0 Hz, 1H, Ar-H), 7.69 (dd, J = 1.1, 8.0 Hz, 1H, Ar-H), 7.54 (dt, J = 1.1, 8.0 Hz, 1H, Ar-H), 7.40 (dt, J = 1.1, 8.0 Hz, 1H, Ar-H), 6.77 (dd, J = 1.9, 7.6 Hz, 1H, Ar-H), 6.67 (dq, J = 2.0, 7.6 Hz, 2H, Ar-H), 6.25 (dd, J = 1.9, 7.6 Hz, 1H, Ar-H), 5.53 (br dd, J = 4.3, 7.9 Hz, 1H, CH), 5.39 (br d, J = 6.4 Hz, 1H, NH), 3.90 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.08 (dd, J = 4.3, 15.3 Hz, 1H, CH_2), 2.86 (dd, J = 7.9, 15.3 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1 (Cq, CO), 148.8, 146.9, 137.8, 135.7 (Cq), 133.7, 128.4, 128.3, 125.0, 121.1, 117.5, 110.8, 109.6 (C-Ar), 55.6, 52.0 (OCH_3), 50.3 (CH), 41.5 (CH_2). MS (ESI): *m/z* 330 (M^+), 257, 207, 123, 108.

4-(2-(methoxycarbonyl)-1-(4-methoxyphenylamino)ethyl)-2-bromophenyl trifluoro-methanesulfonate (9d): Potassium *tert*-butoxide (22.4 mg, 0.2 mmol) was added to a solution of (*E*)-3-bromo-4-trifluoromethylsulfonyloxycinnamaldehyde (357 mg, 1 mmol), nitrosobenzene (117 mg, 1.1 mmol) and the catalyst (85 mg, 0.2 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed under vacuum, and the residue was diluted with methanol (3 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 2.2 Hz, 2H, Ar-H), 7.42 (dd, J = 2.2, 8.5 Hz, 1H, Ar-H), 7.29 (d, J = 8.5 Hz, 2H, Ar-H), 6.73 (AB, d, J_{AB} = 8.9 Hz, 2H, Ar-H), 6.48 (AB, d, J_{AB} = 8.8 Hz, 2H, Ar-H), 4.74 (dd, J = 6.2, 6.5 Hz, 1H, CH), 4.38 (br s, 1H, NH), 3.72 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 2.78 (ddd, J = 3.9, 6.2, 6.5 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1 (Cq, CO), 164.6 (d, J = 12.5 Hz), 162.1 (d, J = 12.5 Hz), 152.6, 151.6, 147.1 (d, J = 15.4 Hz), 140.3, 115.1, 114.8, 109.2 (d, J = 25.4 Hz), 102.9 (t, J = 25.4 Hz), 55.7, 55.3 (OCH_3), 52.0 (CH), 42.3 (CH_2). MS (ESI): *m/z* 513 (M^+), 440, 305, 122.

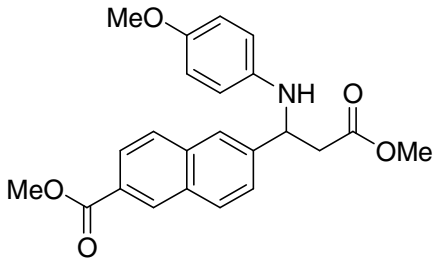
Methyl 4-(2-methoxycarbonyl)-1-(4-methoxyphenylamino)ethyl)benzoate (9e): Potassium *tert*-butoxide (22.4 mg, 0.2 mmol) was added to a solution of (*E*)-4-methoxycarbonylcinnamaldehyde (190 mg, 1 mmol), nitrosobenzene (117 mg, 1.1 mmol) and the catalyst (85 mg, 0.2 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed under vacuum, and the residue was diluted with methanol (3 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (AB, J_{AB} = 8.2 Hz, 2H, Ar-H), 7.45 (AB, J_{AB} = 8.2 Hz, 2H, Ar-H), 6.69 (AB, d, J_{AB} = 8.4 Hz, 2H, Ar-H), 6.50 (AB, d, J_{AB} = 8.4 Hz, 2H, Ar-H), 4.81 (br t, J = 6.6 Hz, 1H, CH), 4.25 (br s, 1H, NH), 3.90 (s, 3H, CH_3), 3.69 (s, 3H, CH_3), 3.65 (s, 3H, CH_3), 2.80 (dd, J = 1.5, 6.6 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4,

166.8 (Cq, CO), 152.5, 147.8, 140.5, 129.4 (Cq), 130.1, 126.4, 115.2, 114.8 (C-Ar), 55.7, 55.6, 52.1, 52.0 (OCH_3, CH), 42.3 (CH_2). MS (ESI): *m/z* 343 (M^+), 270, 122, 108.

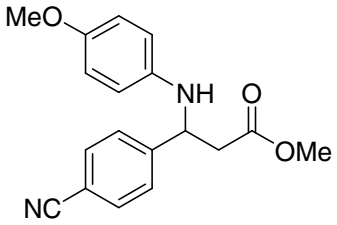
Methyl 6-(2-methoxycarbonyl)-1-(4-methoxyphenylamino)ethyl)naphthalene-2-carboxylate (9f): Potassium *tert*-butoxide (22.4 mg, 0.2 mmol) was added to a solution of methyl (*E*)-6-(2-formylvinyl)naphthalene-2-carboxylate (240 mg, 1 mmol), nitrosobenzene (117 mg, 1 mmol) and the catalyst (85 mg, 0.2 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed under vacuum, and the residue was diluted with methanol (3 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (s, 1H, Ar-H), 8.05 (dd, J = 1.7, 8.5 Hz, 1H, Ar-H), 7.93 (d, J = 8.5 Hz, 1H, Ar-H), 7.88 (s, 1H, Ar-H), 7.84 (d, J = 8.5 Hz, 1H, Ar-H), 7.57 (dd, J = 1.7, 8.5 Hz, 1H, Ar-H), 6.69 (AB, d, J_{AB} = 8.4 Hz, 2H, Ar-H), 6.57 (AB, d, J_{AB} = 8.4 Hz, 2H, Ar-H), 4.94 (dd, J = 5.2, 6.7 Hz, 1H, CH), 4.30 (br s, 1H, NH), 3.98 (s, 3H, CH_3), 3.68 (s, 3H, CH_3), 3.67 (s, 3H, CH_3), 2.84 (dd, J = 3.0, 5.2, 6.7 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 167.2 (Cq, CO), 152.4, 142.7, 140.7, 135.6, 132.0 (Cq), 130.8, 130.1, 128.2 (C-Ar), 127.3 (Cq), 125.6, 125.2, 125.0 (C-Ar), 115.2, 114.8 (C-Ar), 56.0, 55.7, 52.0 (OCH_3), 52.3 (CH), 42.5 (CH_2).

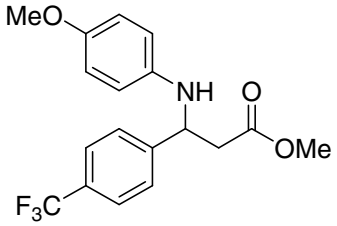
Methyl 3-(4-methoxyphenylamino)-3-(4-cyanophenyl)propanoate (9g): Potassium *tert*-butoxide (22.4 mg, 0.2 mmol) was added to a solution of (*E*)-4-cyanocinnamaldehyde (157 mg, 1 mmol), nitrosobenzene (117 mg, 1.1 mmol) and the catalyst (85 mg, 0.2 mmol) in

dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed under vacuum, and the residue was diluted with methanol (3 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.



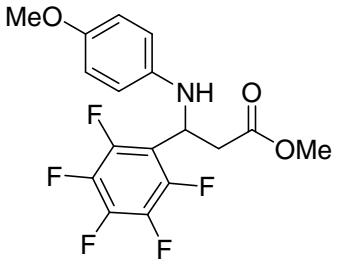
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (AB, d, J_{AB} = 8.4 Hz, 2H, Ar-H), 7.51 (AB, d, J_{AB} = 8.4 Hz, 2H, Ar-H), 6.71 (AB, d, J_{AB} = 9.0 Hz, 2H, Ar-H), 6.47 (AB, d, J_{AB} = 9.0 Hz, 2H, Ar-H), 4.80 (dd, J = 4.5, 6.5 Hz, 1H, CH), 4.38 (br s, 1H, NH), 3.71 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 2.81 (ddd, J = 2.7, 4.5, 6.5 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1 (Cq, CO), 152.7, 148.1, 140.1 (Cq), 132.7, 127.2 (C-Ar), 118.7 (Cq), 111.4 (Cq, CN), 115.2, 114.8 (C-Ar), 55.7, 55.5 (OCH_3), 52.1 (CH), 42.1 (CH_2). MS (ESI): *m/z* 310 (M^+), 237, 122.

Methyl 3-(4-methoxyphenylamino)-3-(4-trifluoromethyl)phenyl)propanoate (9h): Potassium *tert*-butoxide (22.4 mg, 0.2 mmol) was added to a solution of (*E*)-4-trifluoromethylcinnamaldehyde (200 mg, 1 mmol), nitrosobenzene (117 mg, 1.1 mmol) and the catalyst (85 mg, 0.2 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed under vacuum, and the residue was diluted with methanol (2 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (AB, J_{AB} = 8.4 Hz, 2H, Ar-H), 7.51 (AB, J_{AB} = 8.4 Hz, 2H, Ar-H), 6.72 (AB, d, J_{AB} = 8.4 Hz, 2H, Ar-H), 6.51 (AB, d, J_{AB} = 8.4 Hz, 2H, Ar-H), 4.81 (dd, J = 3.4, 6.7 Hz, 1H, CH), 4.20 (br s, 1H, NH), 3.71 (s, 3H, CH_3), 3.68 (s, 3H, CH_3), 2.82 (ddd, J = 1.7, 3.4, 6.7 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3 (Cq, CO), 152.6, 146.6, 140.4 (Cq), 129.7 (q, J = 32.0 Hz, Cq,), 126.7 (C-Ar), 125.8 (q, J = 3.8 Hz, C-Ar), 125.6 (q, J_{CF} = 270.4 Hz, Cq, CF_3), 115.2, 114.8 (C-Ar), 55.6, 55.5 (OCH_3), 52.0 (CH), 42.4 (CH_2). MS (ESI): *m/z* 353 (M^+), 280, 122, 108.

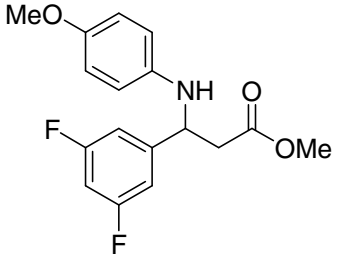
Methyl 3-(4-methoxyphenylamino)-3-(perfluorophenyl)propanoate (9i): Potassium *tert*-butoxide (22.4 mg, 0.2 mmol) was added to a solution of (*E*)-pentafluorocinnamaldehyde (222 mg, 1 mmol), nitrosobenzene (117 mg, 1.1 mmol) and the catalyst (85 mg, 0.2 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed under vacuum, and the residue was diluted with methanol (2 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.



^{1}H NMR (400 MHz, $CDCl_3$): δ 6.75 (AB, d, J_{AB} = 9.0 Hz, 2H, Ar-H), 6.64 (AB, d, J_{AB} = 9.0 Hz, 2H, Ar-H), 5.32 (br t, J = 7.5 Hz, 1H, CH), 3.96 (br s, 1H, NH), 3.72 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.09 (dd, J = 7.5, 15.3 Hz, 1H, CH_2), 2.93 (dd, J = 7.5, 15.3 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.4 (Cq, CO), 153.4, 146.2 (m), 143.8 (m),

141.7 (m), 138.8 (m), 136.3 (m), 139.4 (Cq), 115.6, 114.9 (C-Ar), 55.5, 52.1 (OCH_3), 47.3 (CH), 39.7 (CH_2). MS (ESI): *m/z* 375 (M^+), 302, 122.

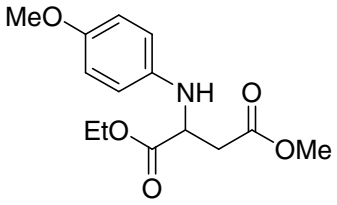
Methyl 3-(4-methoxyphenylamino)-3-(3,5-difluorophenyl)propanoate (9j): Potassium *tert*-butoxide (22.4 mg, 0.2 mmol) was added to a solution of (*E*)-3,5-difluorocinnamaldehyde (168 mg, 1 mmol), nitrosobenzene (117 mg, 1.1 mmol) and the catalyst (85 mg, 0.2 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed under vacuum, and the residue was diluted with methanol (2 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.



^{1}H NMR (400 MHz, $CDCl_3$): δ 6.93 (dd, J = 2.2, 8.0 Hz, 2H, Ar-H), 6.73 (AB, d, J_{AB} = 8.8 Hz, 2H, Ar-H), 6.70–6.66 (m, 1H, Ar-H), 6.51 (AB, d, J_{AB} = 8.8 Hz, 2H, Ar-H), 4.72 (dd, J = 5.6, 7.6 Hz, 1H, CH), 4.34 (br s, 1H, NH), 3.73 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 2.78 (ddd, J = 5.6, 5.8, 7.6 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.0 (Cq, CO), 152.8, 146.0, 144.7, 140.0 (Cq), 132.2, 127.0, 123.1, 115.2, 114.9 (CH), 55.7, 54.8 (OCH_3), 52.1 (CH), 42.3 (CH_2). MS (ESI): *m/z* 321 (M^+), 248, 122.

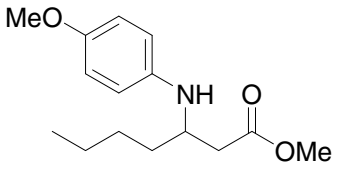
1-Ethyl 4-methyl 2-(4-methoxyphenylamino)succinate (9k): Potassium *tert*-butoxide (22.4 mg, 0.2 mmol) was added to a solution of (*E*)-ethyl 3-formylacrylate (128 mg, 1 mmol), nitrosobenzene (117 mg, 1.1 mmol) and the catalyst (85 mg, 0.2 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed under vacuum, and the residue was diluted with methanol (2 mL),

followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.



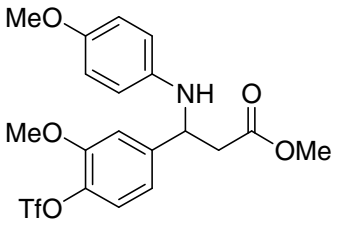
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (AB, d, J_{AB} = 8.9 Hz, 2H, Ar-H), 6.67 (AB, d, J_{AB} = 8.9 Hz, 2H, Ar-H), 4.36 (t, J = 6.0 Hz, 1H, CH), 4.20 (dq, J = 2.5, 7.1 Hz, 2H, CH_2), 3.75 (s, 3H, CH_3), 3.71 (s, 3H, CH_3), 2.85 (d, J = 6.0 Hz, 2H, CH_2), 2.00 (br s, 1H, NH), 1.85 (t, J = 7.1 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 171.1 (Cq, CO), 153.2, 140.1 (Cq), 115.9, 114.8 (C-Ar), 61.6 (OCH_2), 55.7, 54.9 (OCH_3), 52.0 (CH), 37.4 (CH_2), 14.1 (CH_3). MS (ESI): *m/z* 281 (M^+), 208, 148, 134.

Methyl 3-(4-methoxyphenylamino)heptanoate (9l): Potassium *tert*-butoxide (22.4 mg, 0.2 mmol) was added to a solution of (*E*)-hept-2-enal (112 mg, 1 mmol), nitrosobenzene (117 mg, 1.1 mmol) and the catalyst (85 mg, 0.2 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed under vacuum and the residue was diluted with methanol (2 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.

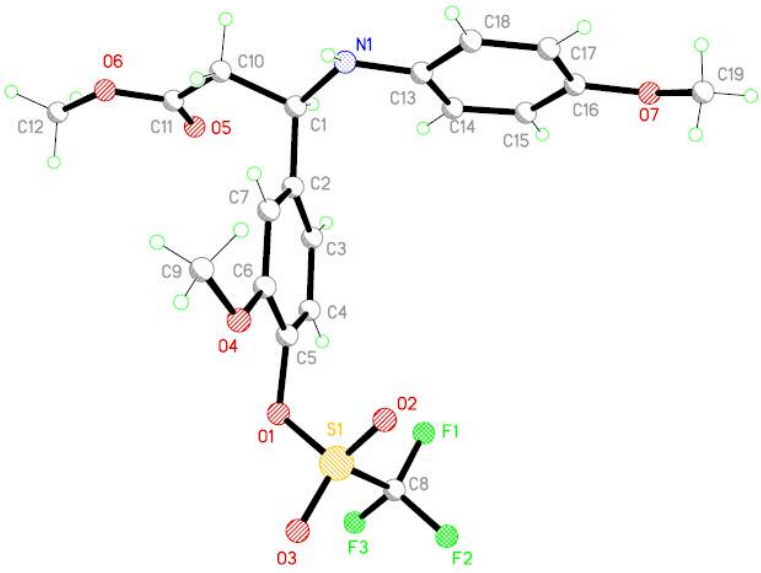


^{1}H NMR (400 MHz, $CDCl_3$): δ 6.78 (AB, d, J_{AB} = 9.0 Hz, 2H, Ar-H), 6.61 (AB, d, J_{AB} = 9.0 Hz, 2H, Ar-H), 3.71 (pentet, J = 6.1 Hz, 1H, CH), 3.75 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.49 (br s, 1H, NH), 2.52 (ddd, J = 5.6, 6.1, 15.1 Hz, 2H, CH_2), 1.60–1.53 (m, 2H, CH_2), 1.47–1.30 (m, 4H, CH_2), 0.90 (br t, J = 6.9 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 152.2, 141.3 (Cq), 115.1, 114.9 (C-Ar), 55.8, 51.6, 51.5 (CH, OCH_3), 39.0, 34.7, 28.3, 22.6 (CH_2), 14.0 (CH_3). MS (ESI): *m/z* 265 (M^+), 208, 192, 148, 134.

4-(2-Methoxycarbonyl)-1-(4-methoxyphenylamino)ethyl-2-methoxyphenyl trifluoromethane sulfonate (12): Potassium *tert*-butoxide (22.4 mg, 0.2 mmol) was added to a solution of (*E*)-3-methoxy-4-trifluoromethylsulfonyloxycinnamaldehyde (310 mg, 1 mmol), nitrosobenzene (117 mg, 1.1 mmol) and the catalyst (85 mg, 0.2 mmol) in dichloromethane (2 mL). The reaction mixture was stirred at room temperature for 6 h. The solvent was removed under vacuum, and the residue was diluted with methanol (2 mL), followed by the addition of perchloric acid (3–5 drops). The mixture was stirred at room temperature overnight. The solvent was removed *in vacuo*, and the residue was diluted with CH_2Cl_2 (5 mL) and saturated aqueous $NaHCO_3$ (10 mL). The aqueous layer was extracted with CH_2Cl_2 (10 mL × 2). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (10 mL) and then brine (10 mL), dried ($MgSO_4$), and concentrated. The pure product was obtained through flash silica gel column chromatography of the residue using hexane and ethyl acetate as the eluents.



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, J = 8.4 Hz, 1H, Ar-H), 7.09 (d, J = 2.0 Hz, 1H, Ar-H), 6.99 (dd, J = 2.0, 8.4 Hz, 1H, Ar-H), 6.73 (AB, d, J_{AB} = 8.8 Hz, 2H, Ar-H), 6.51 (AB, d, J_{AB} = 8.8 Hz, 2H, Ar-H), 4.73 (dd, J = 5.8, 7.6 Hz, 1H, CH), 4.32 (br s, 1H, NH), 3.89 (s, 3H, CH_3), 3.72 (s, 3H, CH_3), 3.68 (s, 3H, CH_3), 2.79 (ddd, J = 5.6, 5.8, 7.6 Hz, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4 (Cq, CO), 152.6, 151.6, 144.4, 140.5, 137.7, 117.3 (q, J_{CF} = 270.4 Hz, Cq, CF_3), 122.6, 117.1, 115.2, 114.8, 111.0, 56.2, 55.6 (OCH_3), 52.0 (CH), 42.5 (CH_2). MS (ESI): *m/z* 463 (M^+), 390, 299, 256, 122.



X-Ray Crystal Structure of **12**.

Table 1. Crystal data and structure refinement for **12**.

Empirical formula	C19 H20 F3 N O7 S	
Formula weight	463.42	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 6.0822(10) Å	α= 69.877(3)°.
	b = 11.4054(18) Å	β= 85.336(3)°.
	c = 16.008(3) Å	γ = 89.285(3)°.
Volume	1039.1(3) $Å^3$	
Z	2	
Density (calculated)	1.481 Mg/m^3	
Absorption coefficient	0.224 mm^{-1}	
F(000)	480	
Crystal size	0.50 × 0.44 × 0.10 mm^3	
Theta range for data collection	1.36 to 26.00°	
Index ranges	-7≤h≤7, -14≤k≤14, -19≤l≤19	
Reflections collected	11953	
Independent reflections	4080 [R(int) = 0.0278]	
Completeness to theta = 26.00°	100.0 %	
Absorption correction	Sadabs, (Sheldrick 2001)	
Max. and min. transmission	0.9779 and 0.8962	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4080 / 0 / 287	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0647, wR2 = 0.1704	
R indices (all data)	R1 = 0.0918, wR2 = 0.1883	
Largest diff. peak and hole	0.646 and -0.187 e.$Å^{-3}$	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **12**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S(1)	6343(1)	-2241(1)	4372(1)	69(1)
O(1)	4756(4)	-1131(2)	4282(1)	69(1)
O(2)	8255(4)	-1891(2)	3784(2)	83(1)
O(3)	6413(5)	-2889(2)	5287(2)	104(1)
O(4)	7902(4)	573(2)	4105(1)	71(1)
O(5)	796(3)	4067(2)	1909(2)	76(1)
O(6)	2297(4)	5203(2)	2592(2)	85(1)
O(7)	9341(5)	922(4)	-1499(2)	130(1)
N(1)	7089(4)	3664(2)	752(2)	66(1)
F(1)	4324(5)	-2618(2)	3124(2)	124(1)
F(2)	5695(4)	-4238(2)	4016(2)	112(1)
F(3)	2779(4)	-3495(2)	4431(2)	121(1)
C(1)	5051(4)	3428(3)	1322(2)	59(1)
C(2)	4988(4)	2193(2)	2103(2)	51(1)
C(3)	3413(5)	1287(3)	2198(2)	67(1)
C(4)	3374(5)	171(3)	2907(2)	68(1)
C(5)	4900(5)	-27(2)	3515(2)	57(1)
C(6)	6509(4)	867(2)	3451(2)	53(1)
C(7)	6528(4)	1973(2)	2732(2)	51(1)
C(8)	4672(7)	-3202(3)	3953(3)	85(1)
C(9)	9344(6)	1524(3)	4132(2)	79(1)
C(10)	4662(5)	4532(3)	1642(2)	62(1)
C(11)	2384(5)	4553(2)	2060(2)	59(1)
C(12)	151(7)	5344(5)	3008(4)	109(2)
C(13)	7659(5)	2935(3)	223(2)	62(1)
C(14)	6166(5)	2215(3)	-4(2)	73(1)
C(15)	6766(6)	1579(4)	-578(3)	83(1)
C(16)	8887(7)	1613(4)	-928(3)	90(1)
C(17)	10381(6)	2303(5)	-709(3)	97(1)
C(18)	9807(5)	2979(4)	-149(2)	83(1)
C(19)	11368(8)	536(5)	-1594(3)	109(1)

Table 3. Bond lengths [Å] and angles [°] for **12**.

S(1)-O(3)	1.398(3)
S(1)-O(2)	1.405(2)
S(1)-O(1)	1.556(2)
S(1)-C(8)	1.825(4)
O(1)-C(5)	1.423(3)
O(4)-C(6)	1.349(3)
O(4)-C(9)	1.417(4)
O(5)-C(11)	1.201(3)
O(6)-C(11)	1.306(4)
O(6)-C(12)	1.449(4)
O(7)-C(19)	1.319(5)
O(7)-C(16)	1.408(5)
N(1)-C(13)	1.398(4)
N(1)-C(1)	1.449(4)
F(1)-C(8)	1.297(4)
F(2)-C(8)	1.305(4)
F(3)-C(8)	1.309(5)
C(1)-C(10)	1.523(4)
C(1)-C(2)	1.526(4)
C(2)-C(3)	1.379(4)
C(2)-C(7)	1.388(4)
C(3)-C(4)	1.383(4)
C(4)-C(5)	1.359(4)
C(5)-C(6)	1.395(4)
C(6)-C(7)	1.385(4)
C(10)-C(11)	1.492(4)
C(13)-C(14)	1.382(5)
C(13)-C(18)	1.385(4)
C(14)-C(15)	1.379(5)
C(15)-C(16)	1.359(5)
C(16)-C(17)	1.353(6)
C(17)-C(18)	1.392(5)
O(3)-S(1)-O(2)	122.61(18)
O(3)-S(1)-O(1)	106.54(16)
O(2)-S(1)-O(1)	112.50(13)
O(3)-S(1)-C(8)	106.22(18)

O(2)-S(1)-C(8)	106.56(19)
O(1)-S(1)-C(8)	99.86(16)
C(5)-O(1)-S(1)	121.93(18)
C(6)-O(4)-C(9)	117.9(2)
C(11)-O(6)-C(12)	117.3(3)
C(19)-O(7)-C(16)	118.9(3)
C(13)-N(1)-C(1)	120.9(3)
N(1)-C(1)-C(10)	108.0(2)
N(1)-C(1)-C(2)	114.1(2)
C(10)-C(1)-C(2)	111.6(3)
C(3)-C(2)-C(7)	119.1(2)
C(3)-C(2)-C(1)	121.0(3)
C(7)-C(2)-C(1)	119.9(2)
C(2)-C(3)-C(4)	120.5(3)
C(5)-C(4)-C(3)	119.4(3)
C(4)-C(5)-C(6)	122.1(3)
C(4)-C(5)-O(1)	119.5(3)
C(6)-C(5)-O(1)	118.2(3)
O(4)-C(6)-C(7)	126.0(2)
O(4)-C(6)-C(5)	116.6(2)
C(7)-C(6)-C(5)	117.4(3)
C(6)-C(7)-C(2)	121.4(2)
F(1)-C(8)-F(2)	109.0(4)
F(1)-C(8)-F(3)	109.4(4)
F(2)-C(8)-F(3)	107.9(3)
F(1)-C(8)-S(1)	110.7(3)
F(2)-C(8)-S(1)	109.5(3)
F(3)-C(8)-S(1)	110.3(3)
C(11)-C(10)-C(1)	113.4(2)
O(5)-C(11)-O(6)	123.4(3)
O(5)-C(11)-C(10)	124.6(3)
O(6)-C(11)-C(10)	111.9(2)
C(14)-C(13)-C(18)	116.6(3)
C(14)-C(13)-N(1)	123.9(3)
C(18)-C(13)-N(1)	119.4(3)
C(15)-C(14)-C(13)	122.0(3)
C(16)-C(15)-C(14)	120.9(4)
C(17)-C(16)-C(15)	118.1(4)

C(17)-C(16)-O(7)	125.3(4)
C(15)-C(16)-O(7)	116.6(4)
C(16)-C(17)-C(18)	122.1(4)
C(13)-C(18)-C(17)	120.2(4)

Symmetry transformations used to generate equivalent atoms:

‘x, y, z’ ‘-x, -y, -z’

Table 4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **12.** The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	79(1)	46(1)	73(1)	-6(1)	-15(1)	-4(1)
O(1)	80(1)	44(1)	67(1)	-4(1)	13(1)	-8(1)
O(2)	66(1)	67(1)	106(2)	-19(1)	-1(1)	-1(1)
O(3)	141(2)	71(2)	81(2)	5(1)	-33(2)	-7(2)
O(4)	96(2)	52(1)	62(1)	-9(1)	-23(1)	-9(1)
O(5)	56(1)	74(2)	103(2)	-37(1)	-12(1)	-12(1)
O(6)	69(2)	90(2)	112(2)	-55(2)	-14(1)	-6(1)
O(7)	93(2)	211(4)	130(3)	-112(3)	-24(2)	31(2)
N(1)	51(1)	65(2)	70(2)	-7(1)	-10(1)	-12(1)
F(1)	176(3)	83(2)	116(2)	-28(2)	-62(2)	-14(2)
F(2)	134(2)	58(1)	148(2)	-38(1)	-11(2)	0(1)
F(3)	88(2)	97(2)	174(3)	-45(2)	-1(2)	-27(1)
C(1)	50(2)	48(2)	70(2)	-8(1)	-11(1)	-4(1)
C(2)	43(1)	45(1)	61(2)	-11(1)	-3(1)	-1(1)
C(3)	55(2)	54(2)	84(2)	-10(2)	-18(2)	-8(1)
C(4)	55(2)	44(2)	93(2)	-10(2)	-6(2)	-11(1)
C(5)	63(2)	38(1)	60(2)	-7(1)	7(1)	-4(1)
C(6)	58(2)	46(2)	53(2)	-16(1)	-4(1)	0(1)
C(7)	52(2)	43(1)	57(2)	-15(1)	2(1)	-10(1)
C(8)	97(3)	52(2)	101(3)	-16(2)	-20(2)	-8(2)
C(9)	98(3)	68(2)	68(2)	-16(2)	-27(2)	-10(2)
C(10)	51(2)	44(2)	83(2)	-9(1)	-16(1)	-7(1)
C(11)	59(2)	39(1)	74(2)	-11(1)	-20(1)	-3(1)
C(12)	97(3)	114(3)	138(4)	-73(3)	9(3)	-9(3)
C(13)	62(2)	60(2)	52(2)	-4(1)	-10(1)	3(1)
C(14)	53(2)	78(2)	77(2)	-14(2)	-3(2)	-2(2)
C(15)	73(2)	91(3)	86(2)	-29(2)	-16(2)	2(2)
C(16)	79(2)	115(3)	81(2)	-38(2)	-23(2)	15(2)
C(17)	66(2)	150(4)	76(2)	-40(3)	-3(2)	16(2)
C(18)	57(2)	107(3)	80(2)	-21(2)	-16(2)	-7(2)
C(19)	121(4)	121(4)	88(3)	-38(3)	-15(3)	24(3)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **12**.

	x	y	z	U(eq)
H(1)	3849	3404	956	71
H(3)	2369	1428	1782	80
H(4)	2313	-439	2968	81
H(7)	7594	2582	2669	62
H(9A)	10323	1791	3597	118
H(9B)	10189	1205	4641	118
H(9C)	8497	2219	4174	118
H(10A)	5713	4504	2073	74
H(10B)	4935	5300	1138	74
H(12A)	-915	5539	2572	164
H(12B)	221	6006	3247	164
H(12C)	-275	4578	3481	164
H(14)	4711	2159	237	87
H(15)	5707	1121	-728	100
H(17)	11840	2328	-940	116
H(18)	10868	3462	-24	100
H(19A)	12369	1240	-1796	164
H(19B)	11443	119	-2023	164
H(19C)	11768	-32	-1030	164
H(1N)	8200(60)	3820(30)	1030(20)	85(11)

Table 6. Hydrogen bonds for **12** [Å and °].

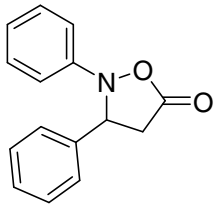
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(5)#1	0.89(4)	2.28(4)	3.166(4)	173(3)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z

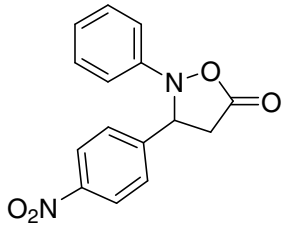
Procedure for the ^{1}H NMR experiments: The base (0.10 mmol) was added under argon to a solution of α,β-unsaturated aldehyde (0.10 mmol), nitrosobenzene (0.11 mmol) and the catalyst (0.02 mmol) in the corresponding deuterated solvent (1 mL). The reaction mixture was stirred at room temperature for 1–3 h. The ^{1}H NMR spectra were recorded directly.

2,3-Diphenylisoxazolidin-5-one (3a):



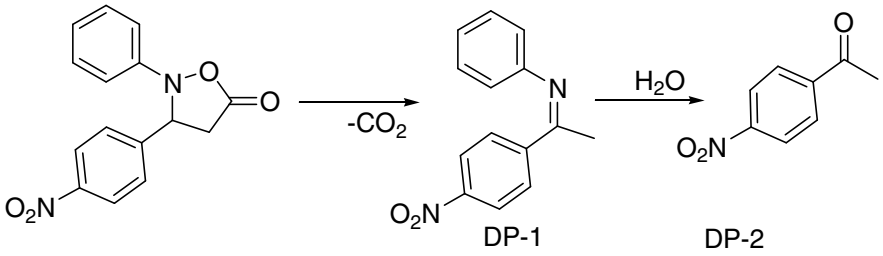
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.00 (m, 10H, Ar-H), 4.77 (dd, J = 7.6, 9.6 Hz, 1H, CH), 3.13 (ddd, J = 7.6, 17.3 Hz, 1H, CH_2), 2.94 (dd, J = 9.6, 17.3 Hz, 1H, CH_2). MS (ESI): *m/z* 239 (M^+), 196, 131, 120, 104.

3-(4-Nitrophenyl)-2-phenylisoxazolidin-5-one (3b):

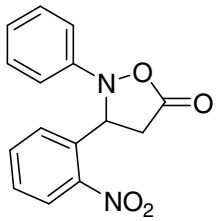


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (AB, d, J_{AB} = 8.8 Hz, 2H, Ar-H), 7.62 (AB, d, J_{AB} = 8.8 Hz, 2H, Ar-H), 7.19–7.05 (m, 4H, Ar-H), 6.98–6.95 (m, 1H, Ar-H), 5.14 (dt, J = 2.5, 6.0 Hz, 1H, CH), 3.12 (dd, J = 6.0, 12.9 Hz, 1H, CH_2), 2.81 (dd, J = 6.0, 12.9 Hz, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8 (Cq, CO), 149.3, 144.9, 135.2 (Cq), 126.6, 124.3, 124.2, 122.8, 120.7 (C-Ar), 62.5 (CH), 38.8 (CH_2). MS (ESI): *m/z* 240, 225, 179, 118, 77.

Degradation of Methyl 3-(4-methoxyphenylamino)-3-(4-nitrophenyl)propanoate (3b): The isoxazolidinone **3b** obtained by the reaction of 4-nitro cinnamaldehyde with nitrosobenzene over NHC was subjected to chromatographic purification. Upon silica gel column chromatography using hexane and ethyl acetate as the eluents, the products imine **DP-1** and **DP-2** obtained were characterized by NMR and mass spectroscopy.

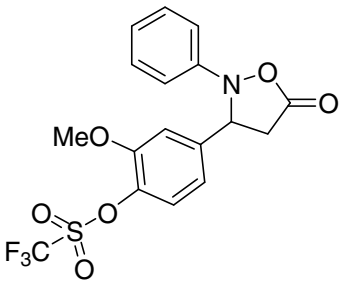


3-(2-Nitrophenyl)-2-phenylisoxazolidin-5-one (3c):



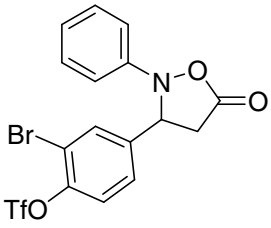
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–6.90 (m, 9H, Ar-H), 5.54 (dd, J = 5.8, 8.7 Hz, 1H, CH), 3.49 (dd, J = 8.7, 17.9 Hz, 1H, CH_2), 2.68 (dd, J = 5.8, 17.9 Hz, 1H, CH_2). *m/z* 284 (M^+), 266, 249, 224, 176, 130, 120, 108, 91, 79.

2-Methoxy-4-(5-oxo-2-phenylisoxazolidin-3-yl)phenyl trifluoromethanesulfonate



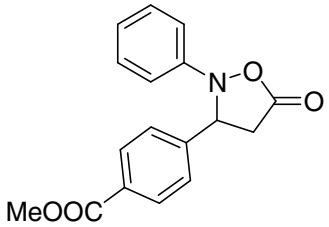
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.00 (m, 8H, Ar-H), 4.84 (dd, J = 8.0, 8.9 Hz, 1H, CH), 3.84 (s, 3H, OCH_3), 3.20 (dd, J = 8.0, 17.3 Hz, 1H, CH_2), 2.92 (dd, J = 8.9, 17.3 Hz, 1H, CH_2). *m/z* 373, 358, 240, 225, 118.

2-Bromo-4-(5-oxo-2-phenylisoxazolidin-3-yl)phenyl trifluoromethanesulfonate (3d)



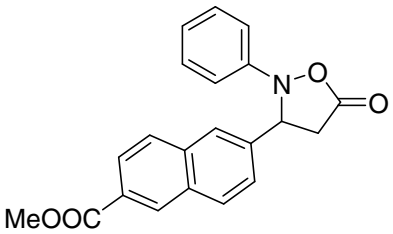
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.07 (m, 8H, Ar-H), 5.15 (dd, J = 7.5, 8.1 Hz, 1H, CH), 3.32 (dd, J = 8.1, 17.3 Hz, 1H, CH_2), 3.04 (dd, J = 7.5, 17.3 Hz, 1H, CH_2). MS (ESI): *m/z* 423, 409, 273, 209, 181, 118, 77.

Methyl 4-(5-oxo-2-phenylisoxazolidin-3-yl)benzoate (3e):



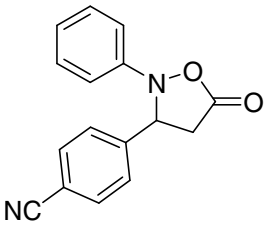
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00–6.93 (m, 9H, Ar-H), 4.84 (dd, J = 7.9, 9.3 Hz, 1H, CH), 3.78 (s, 3H, OCH_3), 3.16 (dd, J = 7.9, 17.3 Hz, 1H, CH_2), 2.91 (dd, J = 9.3, 17.3 Hz, 1H, CH_2). MS (ESI): *m/z* 253, 238, 118, 77.

Methyl 6-(5-oxo-2-phenylisoxazolidin-3-yl)naphthalene-2-carboxylate (3f):



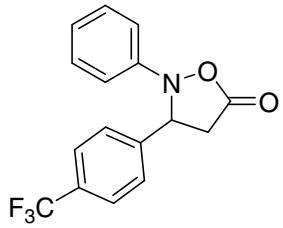
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (s, 1H, Ar-H), 8.10–7.32 (m, 5H, Ar-H), 7.29–7.22 (m, 3H, Ar-H), 7.10–7.04 (m, 2H, Ar-H), 5.18 (dd, J = 7.9, 9.0 Hz, 1H, CH), 3.91 (s, 3H, OCH_3), 3.33 (dd, J = 7.9, 17.2 Hz, 1H, CH_2), 3.13 (dd, J = 9.0, 17.2 Hz, 1H, CH_2).

4-(5-oxo-2-phenylisoxazolidin-3-yl)benzonitrile (3g):



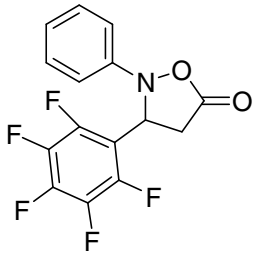
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74–6.87 (m, 9H, Ar-H), 4.86 (br t, J = 8.2 Hz, 1H, CH), 3.20 (dd, J = 8.2, 17.3 Hz, 1H, CH_2), 2.87 (dd, J = 8.2, 17.3 Hz, 1H, CH_2). MS (ESI): *m/z* 220, 205, 118, 77.

3-(4-(Trifluoromethyl)phenyl)-2-phenylisoxazolidin-5-one (3h):



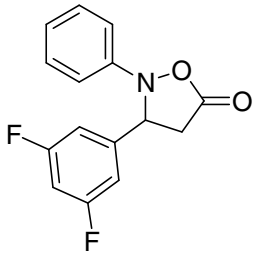
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.00 (m, 9H, Ar-H), 4.87 (dd, J = 8.1, 9.0 Hz, 1H, CH), 3.19 (dd, J = 8.1, 17.3 Hz, 1H, CH_2), 2.90 (dd, J = 9.0, 17.3 Hz, 1H, CH_2). MS (ESI): *m/z* 307 (M^+), 264, 199, 120, 109.

3-(Perfluorophenyl)-2-phenylisoxazolidin-5-one (3i):



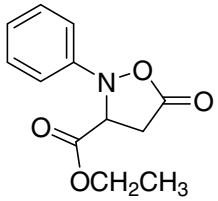
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.20 (m, 5H, Ar-H), 5.25 (dd, J = 6.7, 9.0 Hz, 1H, CH), 3.23 (dd, J = 9.0, 17.5 Hz, 1H, CH_2), 3.11 (dd, J = 6.7, 17.5 Hz, 1H, CH_2). MS (ESI): *m/z* 329 (M^+), 287, 221, 120.

3-(3,5-Difluorophenyl)-2-phenylisoxazolidin-5-one (3j):



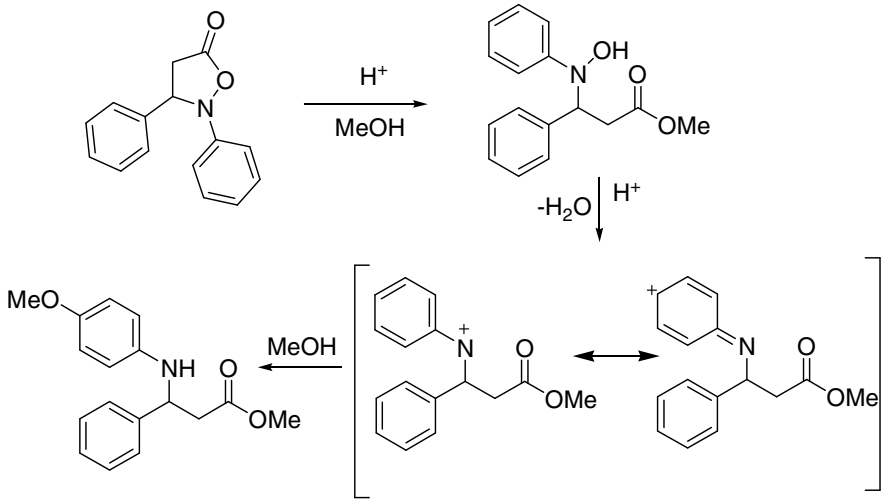
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–6.81 (m, 8H, Ar-H), 5.07 (t, J = 8.0 Hz, 1H, CH), 3.29 (dd, J = 8.0, 17.2 Hz, 1H, CH_2), 3.01 (dd, J = 8.0, 17.2 Hz, 1H, CH_2). MS (ESI): *m/z* 275 (M^+), 232, 167, 120, 109.

Ethyl 5-oxo-2-phenylisoxazolidine-3-carboxylate (3k):

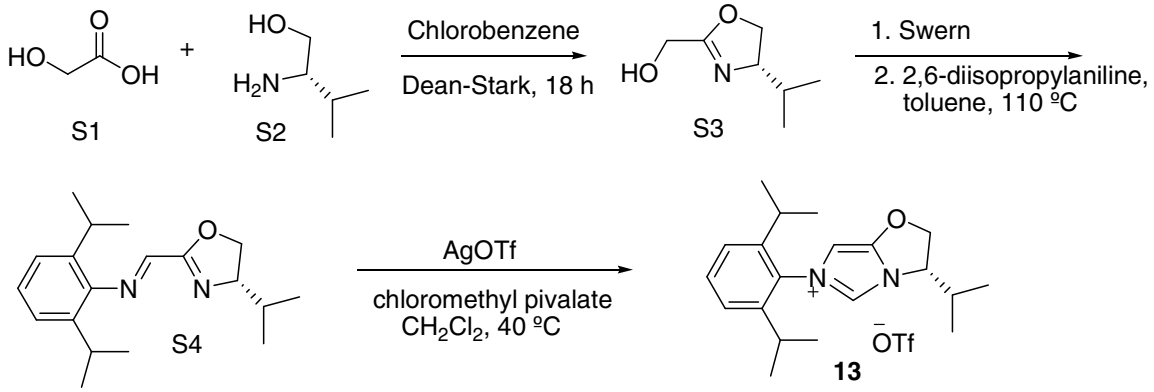


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.00 (m, 5H, Ar-H), 4.62 (dd, J = 4.9, 7.5 Hz, 1H, CH), 4.26 (q, J = 7.0 Hz, 2H, OCH_2), 3.11 (ddd, J = 4.9, 7.5, 17.2 Hz, 2H, CH_2), 1.29 (t, J = 7.0 Hz, 3H, CH_3). MS (ESI): *m/z* 235 (M^+), 207, 162, 134, 120, 99.

Proposed mechanism for the acid-catalyzed conversion of *N*-phenylisoxazolidi-5-ones to *N*-PMP protected *β*-amino acid esters:



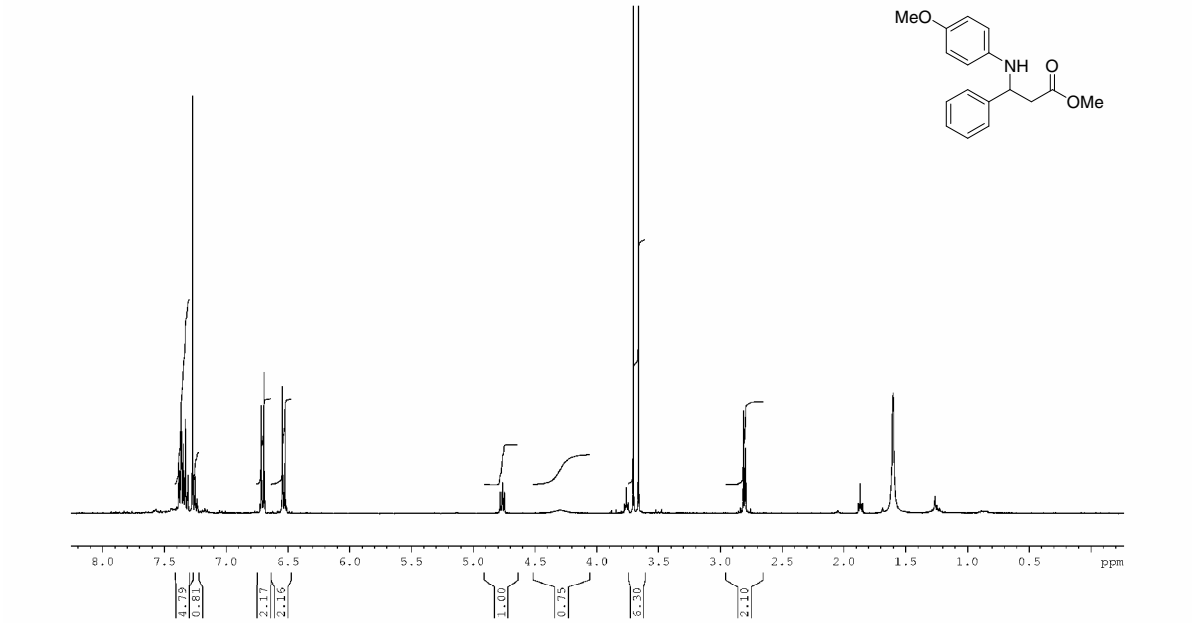
Chiral catalyst synthesis:



A mixture of valinol S**2** (5 g, 48.5 mmol) and glycolic acid S**1** (4.05 g, 53.3 mmol) in chlorobenzene (500 mL) was subjected to Dean-Stark condition for 18 h at 160 °C. The solvent was evaporated and the residue was distilled using Kugelruhr (120 °C, 1 mmHg) to give the alcohol S**3** as white crystal in 70% yield (4.9 g). ^{1}H NMR (400 MHz, $CDCl_3$) of S**3**: δ 4.36 (dd, J = 8.4, 9.5 Hz, 1H, CH_2), 4.25 (br d, J = 2.8 Hz, 2H, CH_2), 4.07 (t, J = 8.3 Hz, 1H, CH_2), 3.93 (m_c, 1H, CH), 3.17 (br s, 1H, OH), 1.76 (octet, J = 6.7 Hz, 1H, CH), 0.99 (d, J = 6.8 Hz, 3H, CH_3), 0.90 (d, J = 6.8 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3 (Cq), 71.4, 70.9 (CH_2), 57.0, 32.4 (CH), 18.8, 18.0 (CH_3). The alcohol S**3** (2 g, 14 mmol) in

CH_2Cl_2 (25 mL) was slowly added to a stirred dichloromethane (150 mL) solution of dimethyl sulfoxide (1.64 g, 21 mmol) and oxalyl chloride (2.7 g, 21 mmol) at -60 °C. After 30 min, triethylamine (4.24 g, 42 mmol) was slowly added at the same temperature. The reaction mixture was warmed within the next 30 min, quenched with water and extracted with dichloromethane (3 times). The combined extracts were washed with water and dried (Na_2SO_4). Without further purification, the aldehyde thus obtained was subjected to imination with 2,6-diisopropylaniline (2.7 g, 15.4 mmol). After refluxing in toluene for 24 h, the solvent was evaporated *in vacuo* from the reaction mixture. The rest of the volatile substance was removed using kugelruhr (140 °C, 1 mmHg) to give the required imine residue S**4**. ^{1}H NMR (400 MHz, $CDCl_3$) of S**4**: δ 7.85 (s, 1H, =CH), 7.18–7.14 (m, 3H, Ar-H), 4.54 (dd, J = 7.9, 9.2 Hz, 1H, CH_2), 4.25–4.15 (m, 2H, CH_2, CH), 2.88 (heptet, J = 7.0 Hz, 2H, CH), 1.91 (octet, J = 6.7 Hz, 1H, CH), 1.17 (d, J = 6.8 Hz, 6H, 2 CH_3), 1.16 (d, J = 6.8 Hz, 6H, 2 CH_3), 1.08 (d, J = 6.8 Hz, 3H, CH_3), 0.98 (d, J = 6.8 Hz, 3H, CH_3). The residual imine was pure enough (95 %) for the cyclization under Glorius condition.[S1]

(S1) Glorius, F.; Altenhoff, G.; Goddard, R.; Lehmann, C. *Chem. Commun.* **2002**, 2704.


MeO
NH
O
OMe
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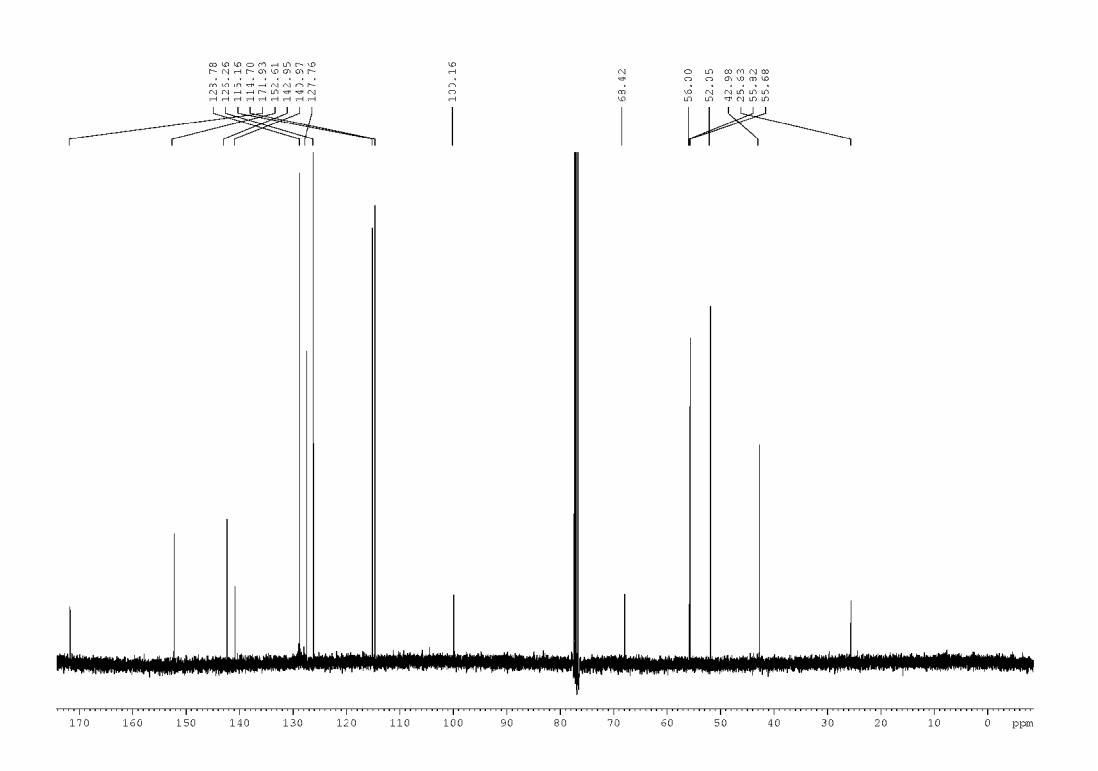
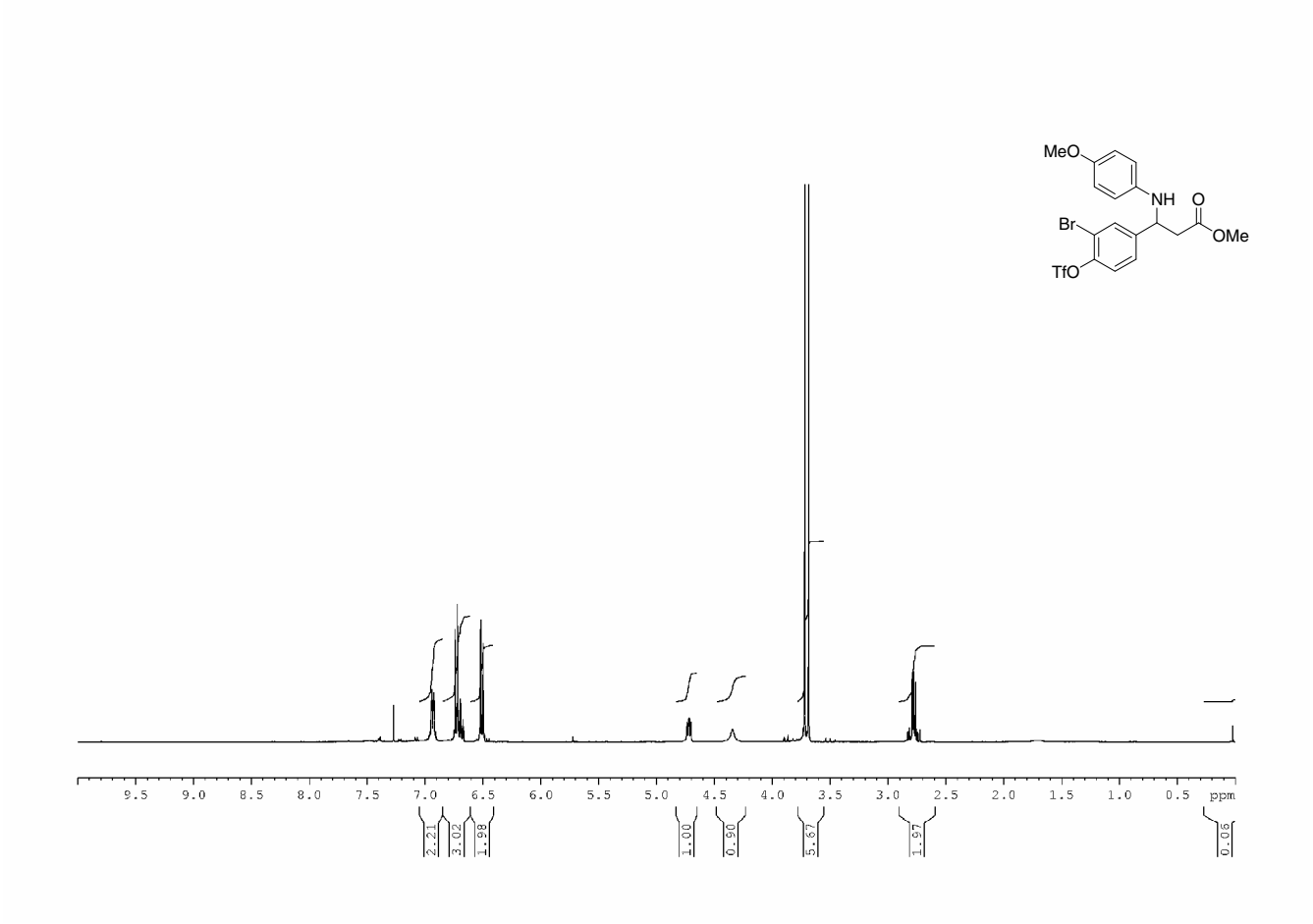
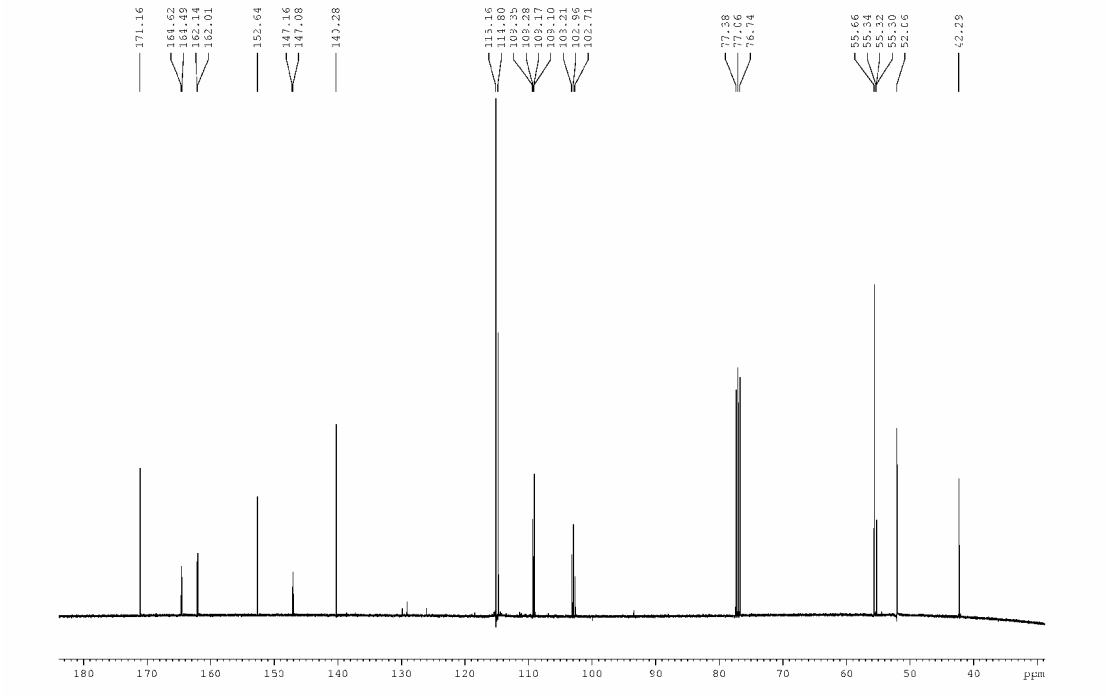
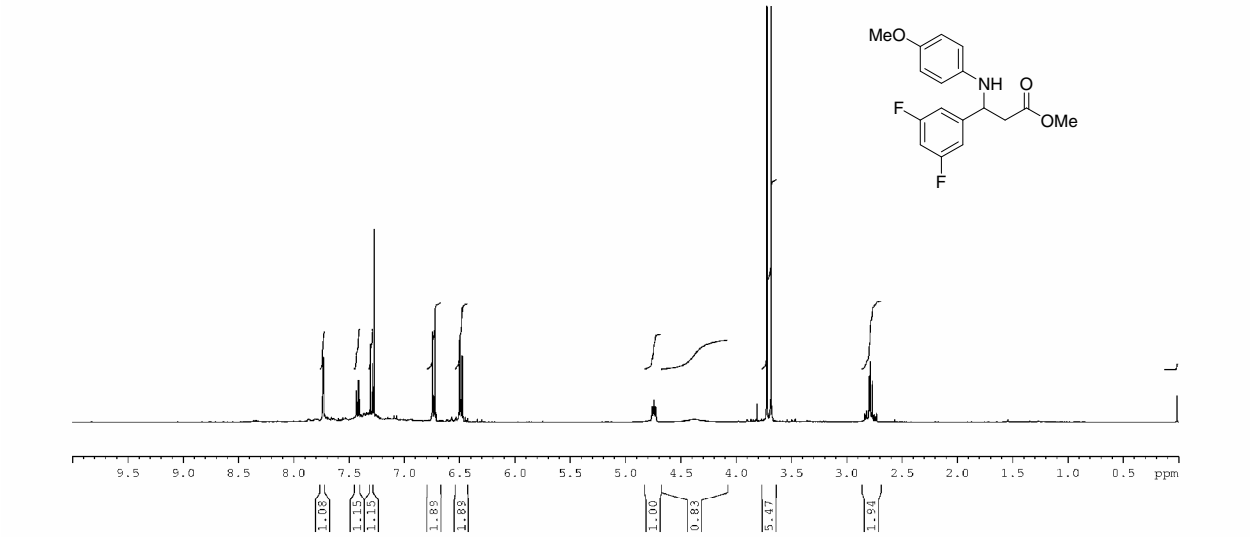
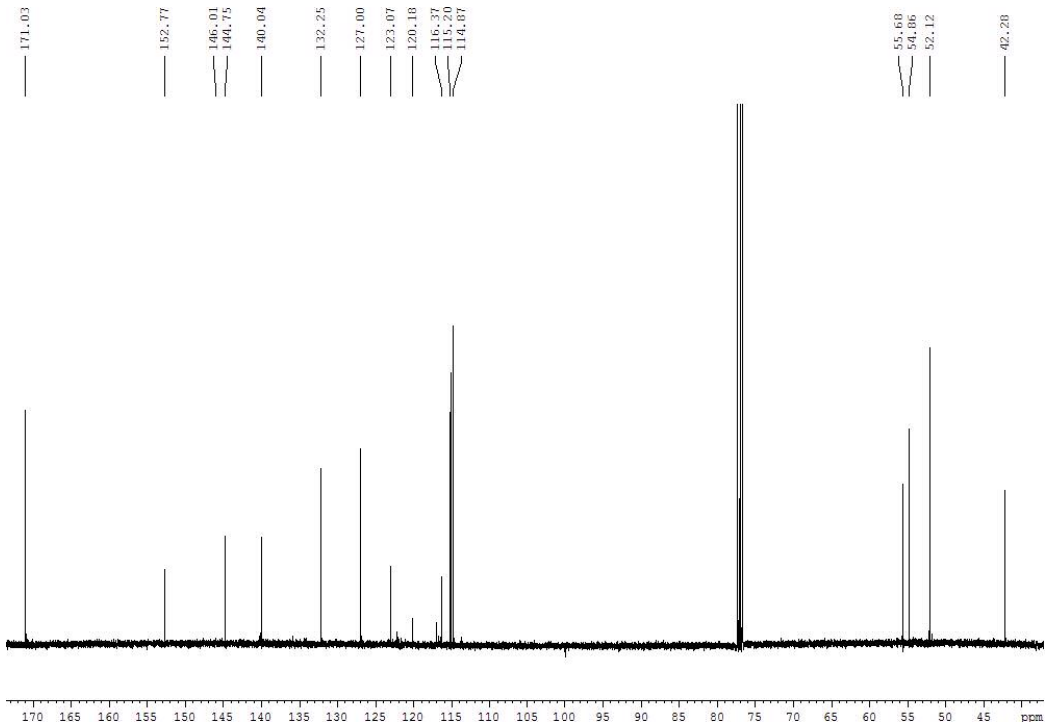
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.79
0.81
2.17
2.16
1.00
0.75
6.30
2.10

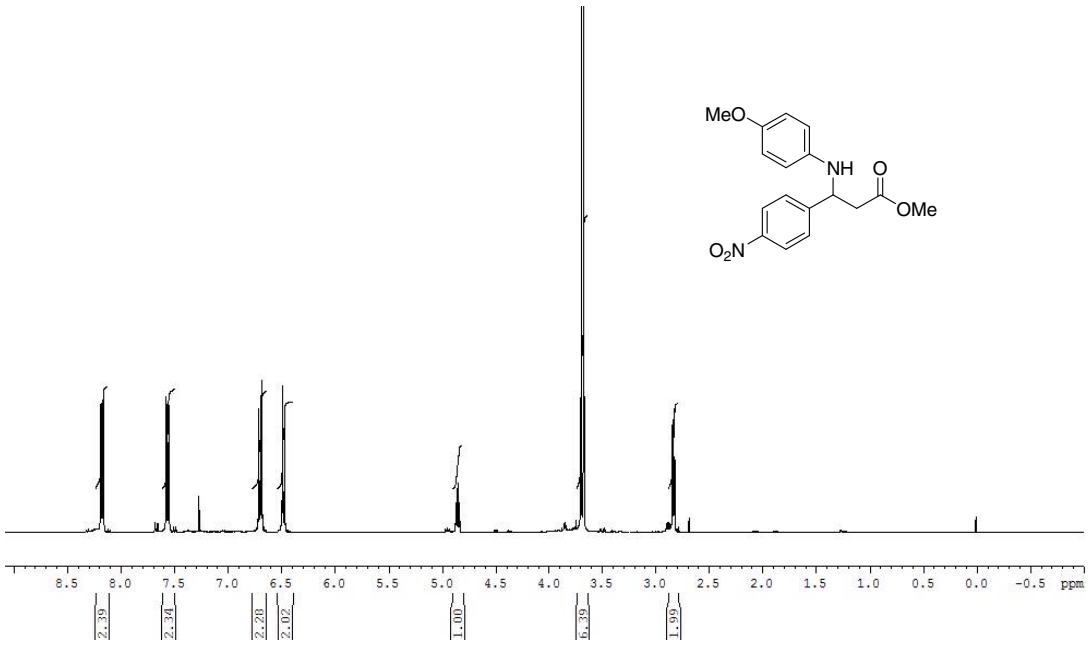

123.78
125.26
115.16
114.70
111.93
152.61
142.95
141.97
127.76
100.16
68.42
56.00
52.05
42.98
25.63
55.22
55.48
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

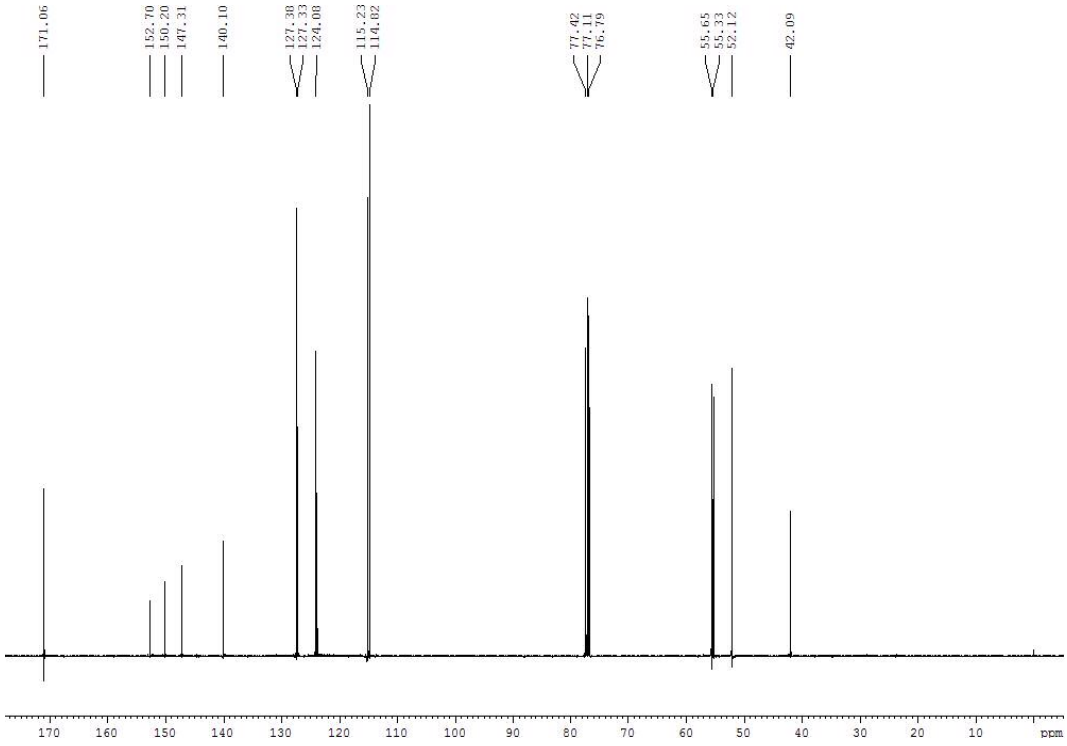

MeO
NH
O
Br
OMe
TfO
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.21
3.02
1.98
1.00
0.90
5.67
1.97
0.06

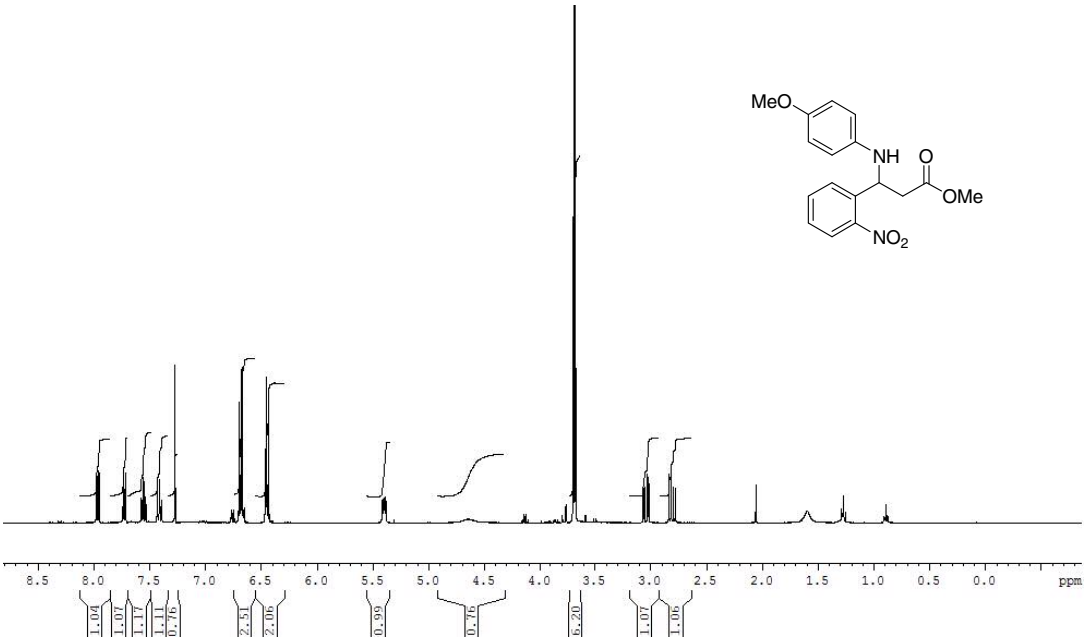

171.16
164.62
164.49
162.14
162.01
152.64
147.16
147.08
143.28
115.16
114.80
109.35
109.28
109.17
109.10
103.21
102.96
102.71
77.38
77.06
76.74
55.66
55.34
55.32
55.30
52.66
42.29
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 ppm

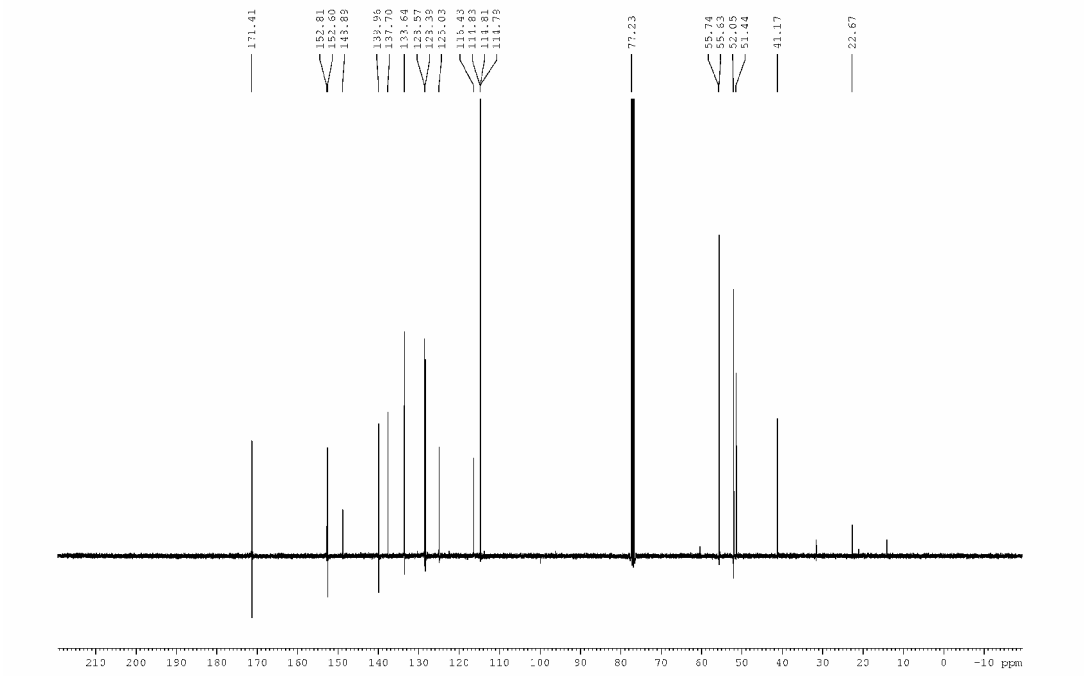

MeO
NH
O
OMe
F
F
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.08
1.15
1.15
1.89
1.88
1.00
0.83
5.47
1.94


171.03
152.77
146.01
144.75
140.04
132.25
127.00
123.07
120.18
116.37
115.20
114.87
55.68
54.86
52.12
42.28
170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 ppm


MeO
NH
O
OMe
O2N
8.5 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 0.5 0.0 -0.5 ppm
2.39
2.34
2.28
2.02
1.00
6.39
1.99


171.06
152.70
150.20
147.31
140.10
127.38
127.33
124.08
115.23
114.82
77.42
77.11
76.79
55.65
55.33
52.12
42.09
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


MeO
NH
O
OMe
NO2
8.5 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 0.5 0.0 ppm
1.04 1.07 1.17 1.11 0.76 2.51 2.06 0.99 0.76 6.20 1.07 1.06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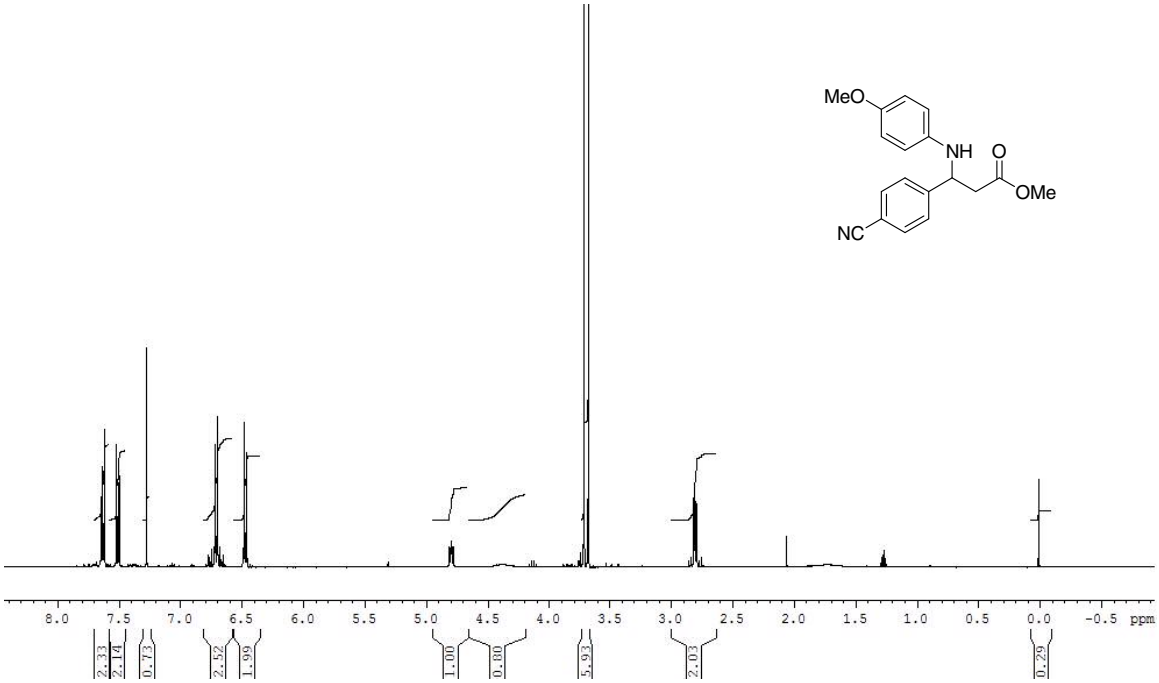
152.60
149.89
138.95
137.70
133.64
131.57
123.39
125.03
116.43
111.83
111.81
111.79
77.23
55.74
55.63
52.05
51.44
41.17
22.67
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm


MeO
NH
O
OMe
NC
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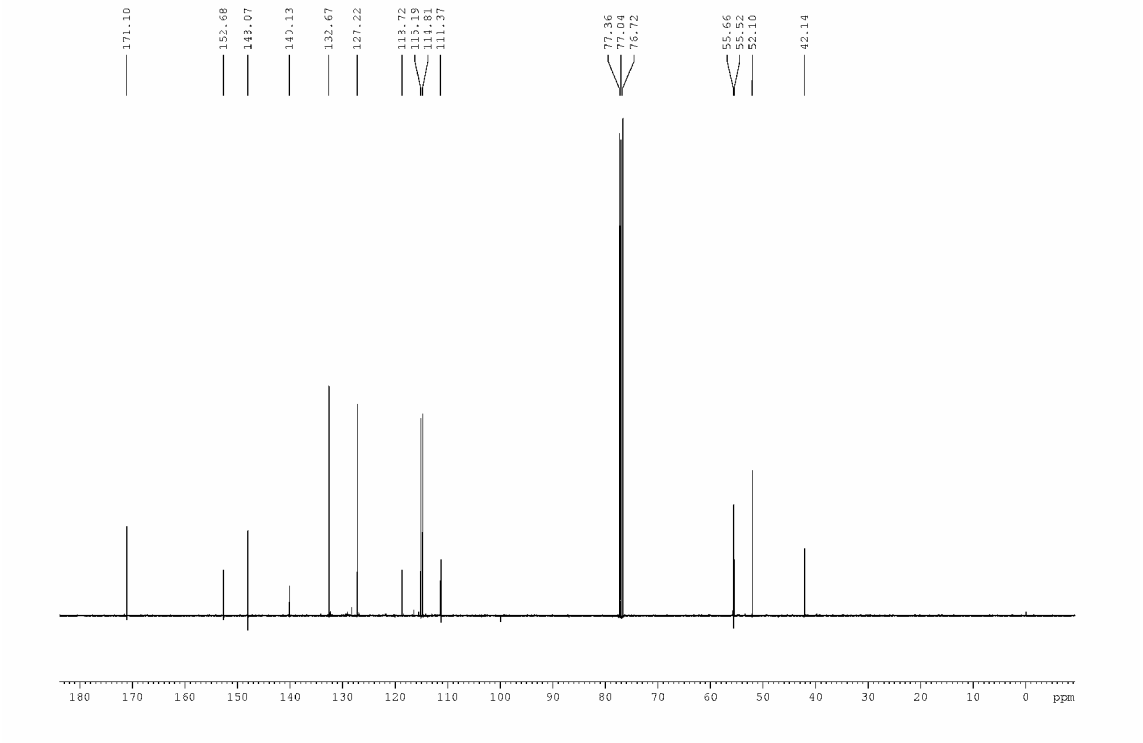
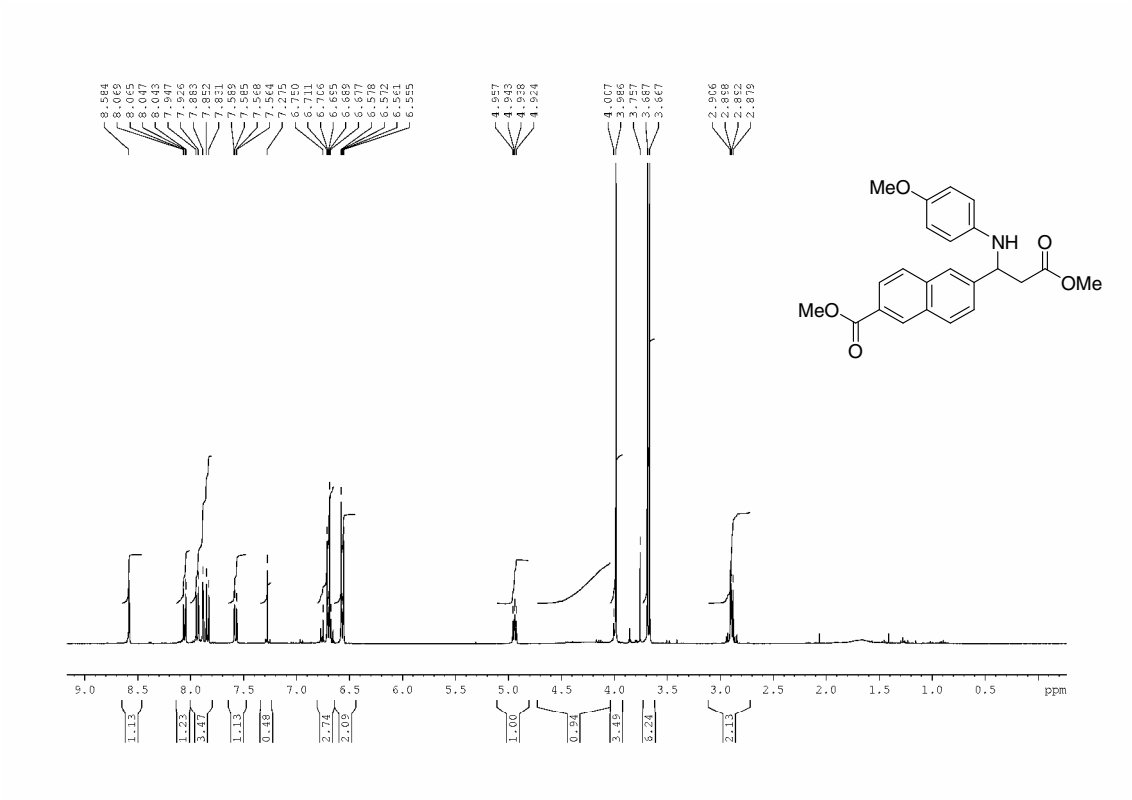
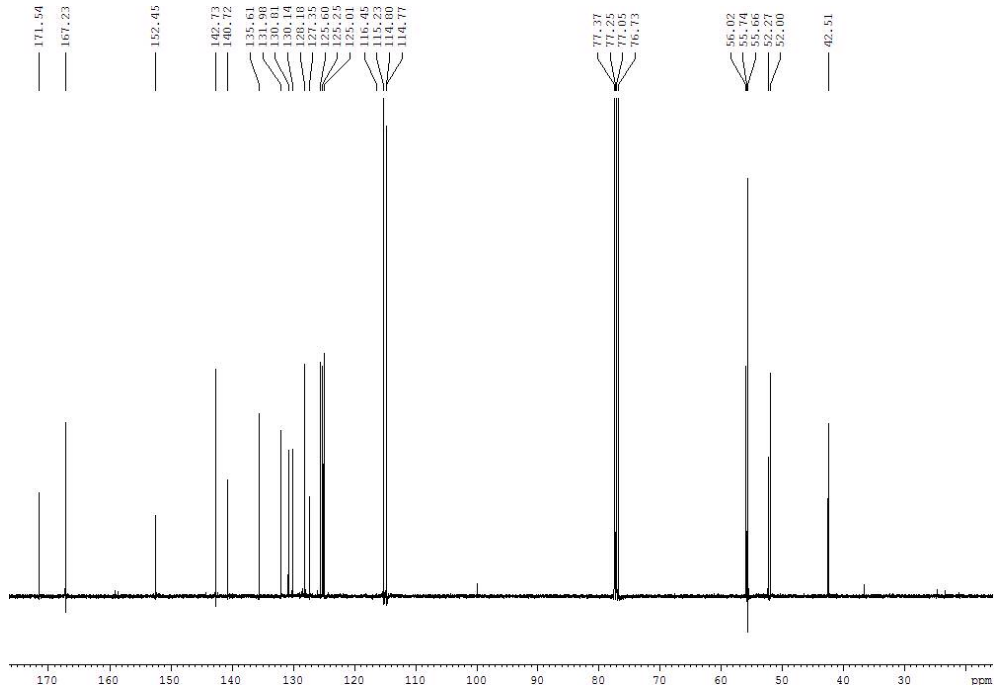
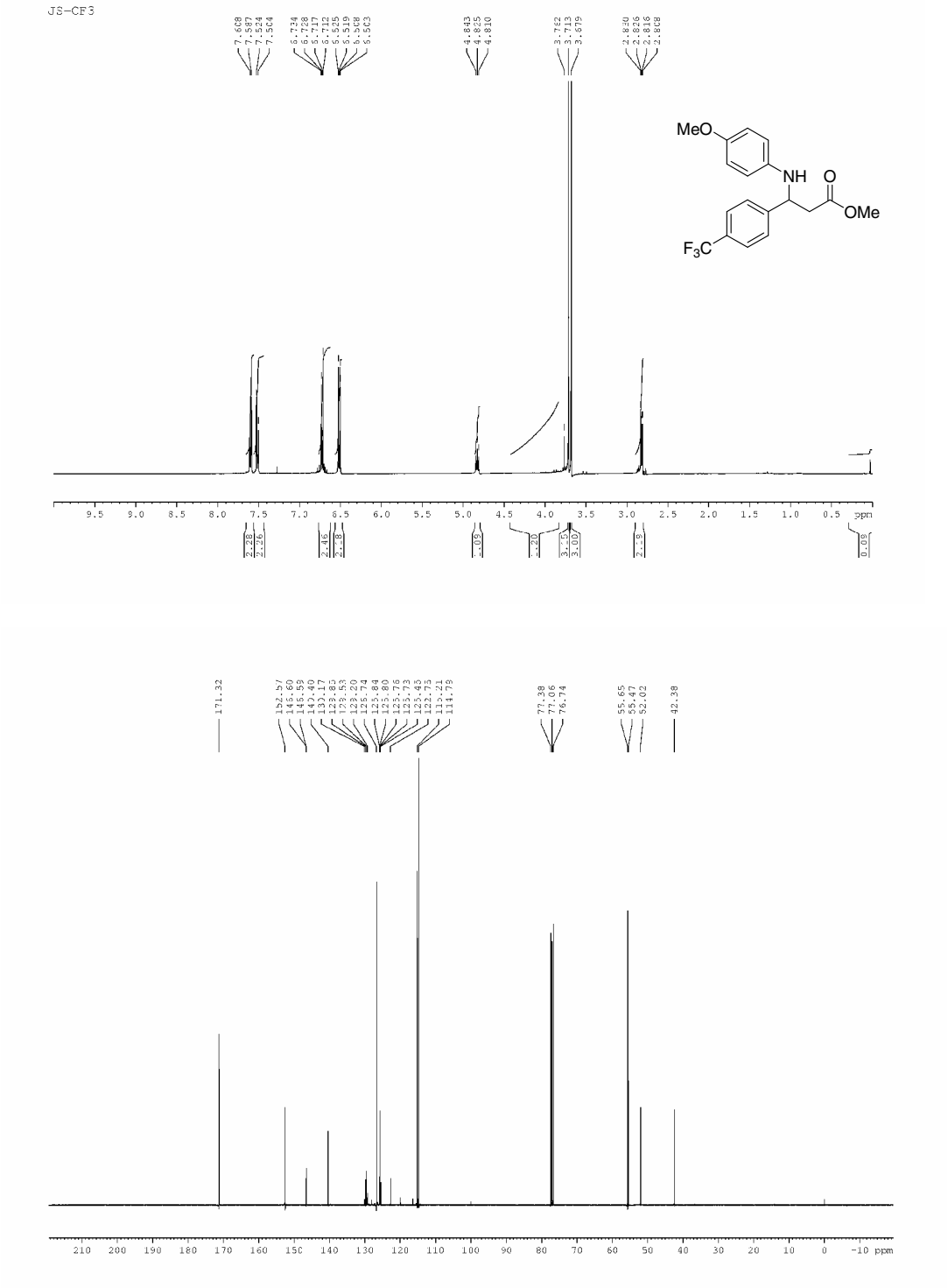
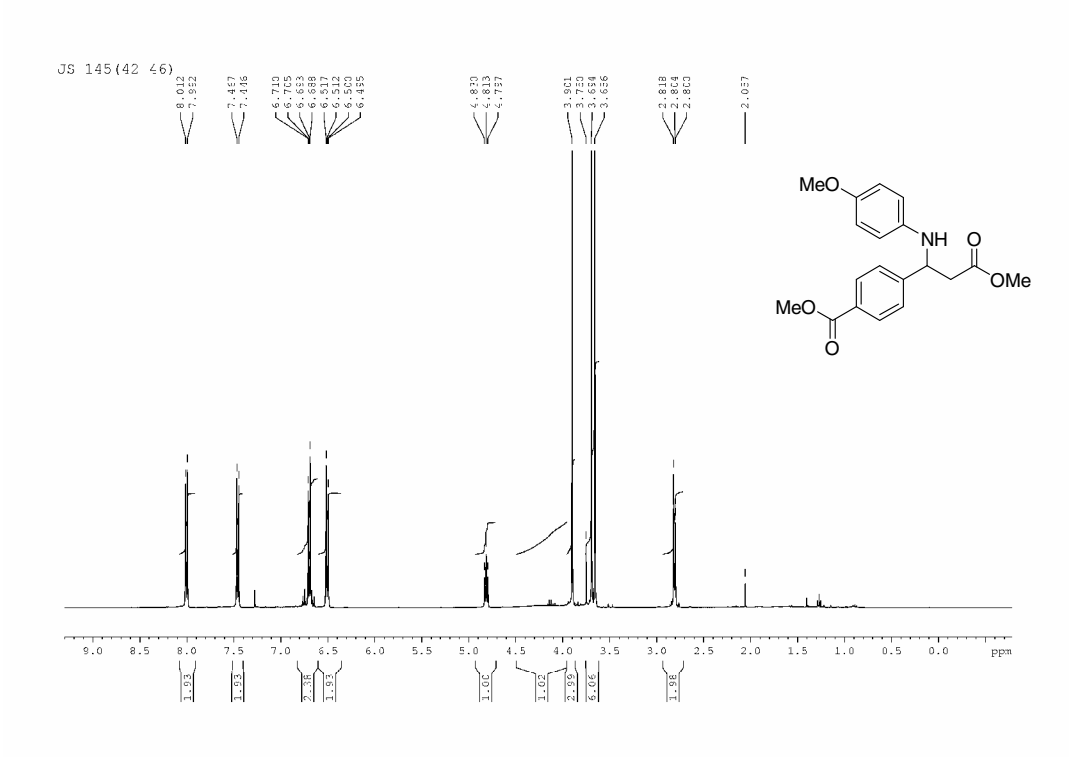
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
2.33
2.14
0.73
2.52
1.99
1.00
0.80
5.93
2.03
0.29

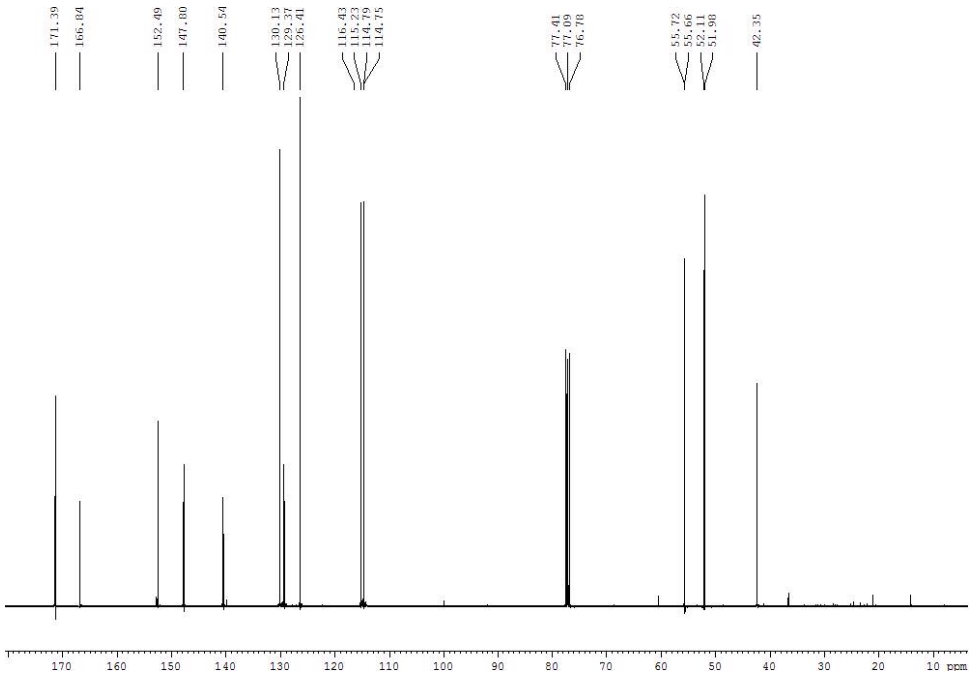

171.10
152.68
143.07
143.13
132.67
127.22
113.72
115.19
114.81
111.37
77.36
77.04
76.72
55.66
55.52
52.10
42.14
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

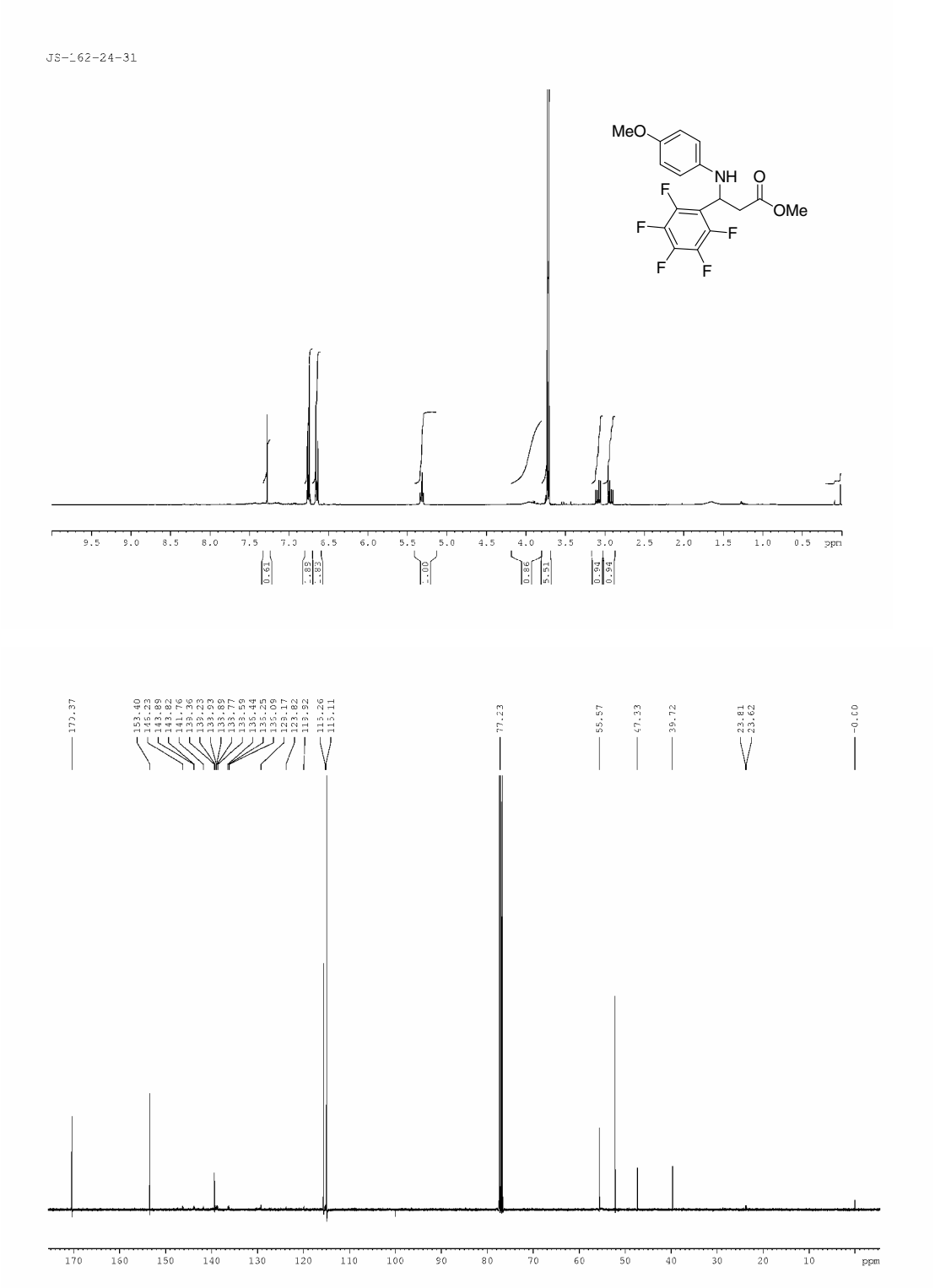

8.584
8.065
8.047
8.043
7.947
7.926
7.883
7.852
7.831
7.589
7.585
7.568
7.564
7.275
6.750
6.711
6.706
6.655
6.689
6.677
6.578
6.572
6.561
6.555
4.957
4.943
4.938
4.924
4.007
3.986
3.757
3.687
3.667
2.906
2.858
2.852
2.879
MeO
NH
O
OMe
MeO
O
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.13
1.23
3.47
1.13
0.48
2.74
2.09
1.00
0.94
3.49
6.24
2.13

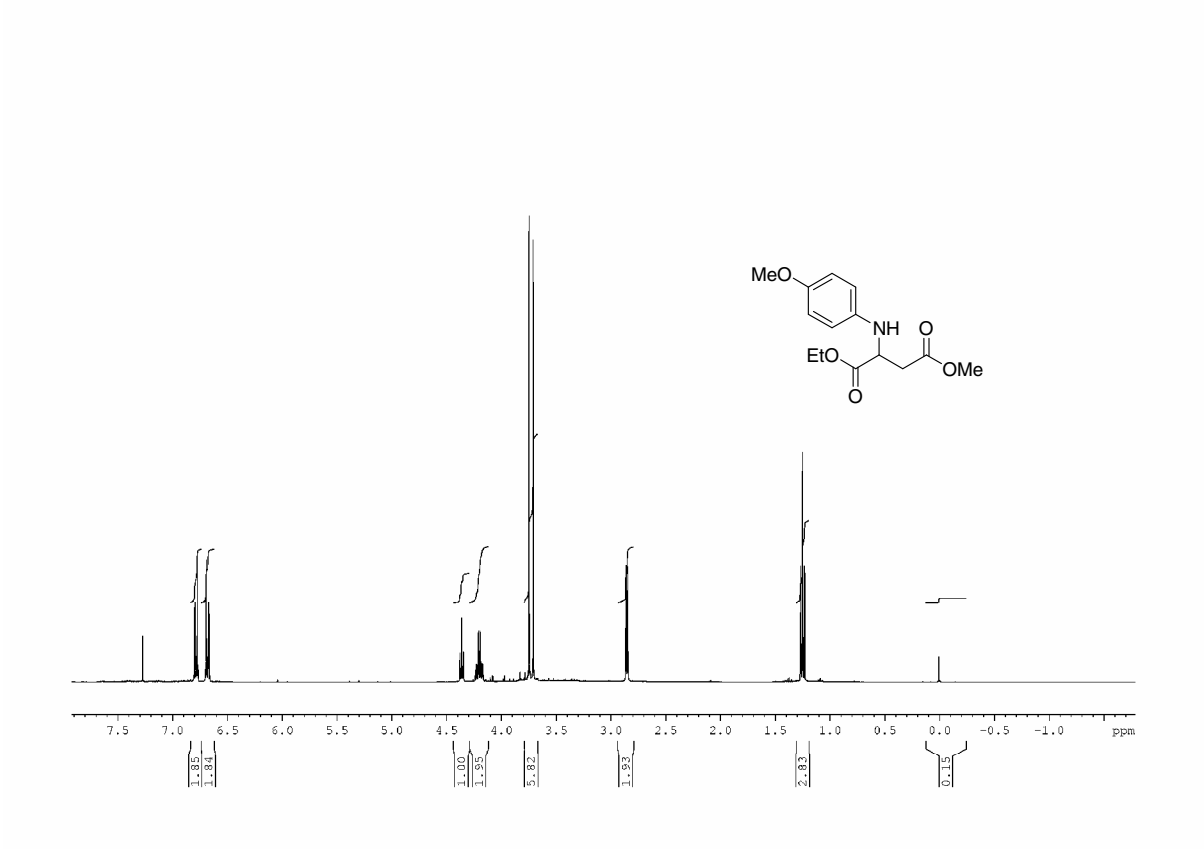

171.54
167.23
152.45
142.73
140.72
135.61
131.98
130.81
130.14
128.18
127.35
125.60
125.25
125.01
116.46
115.23
114.90
114.77
77.37
77.25
77.05
76.73
56.02
55.74
55.66
52.27
52.00
42.51
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

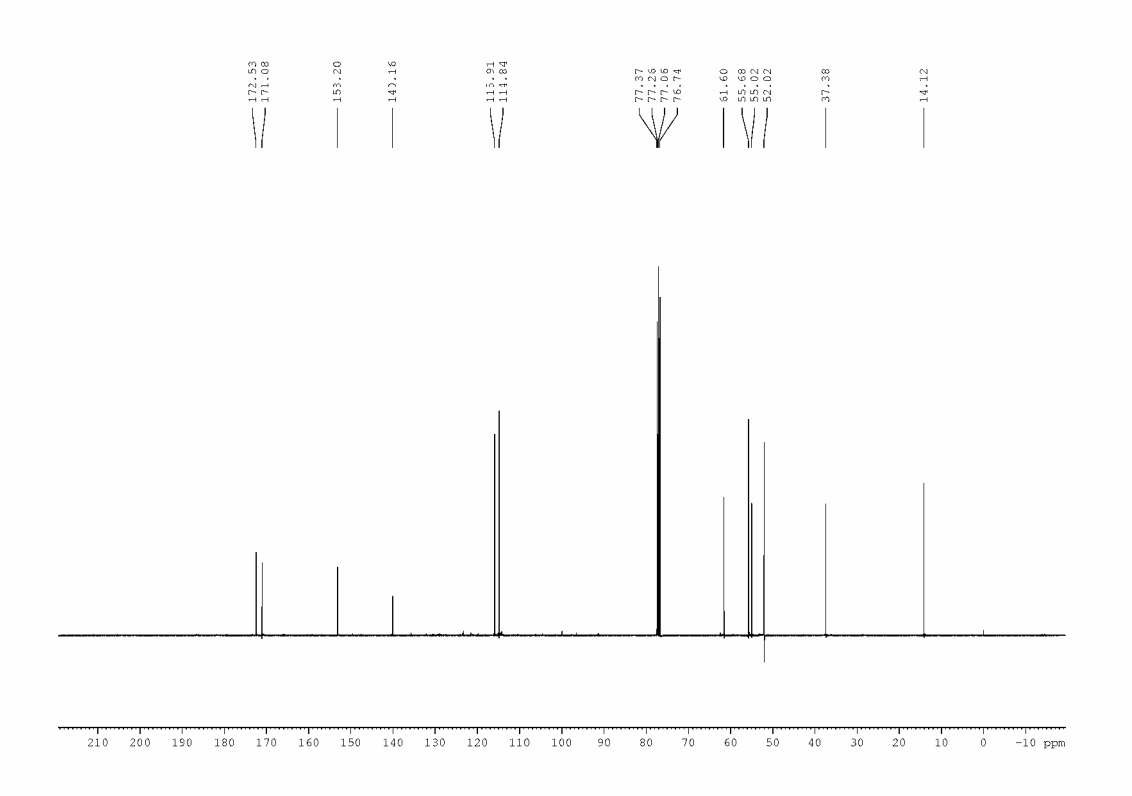

JS-CF3
MeO
NH
O
OMe
F3C
ppm

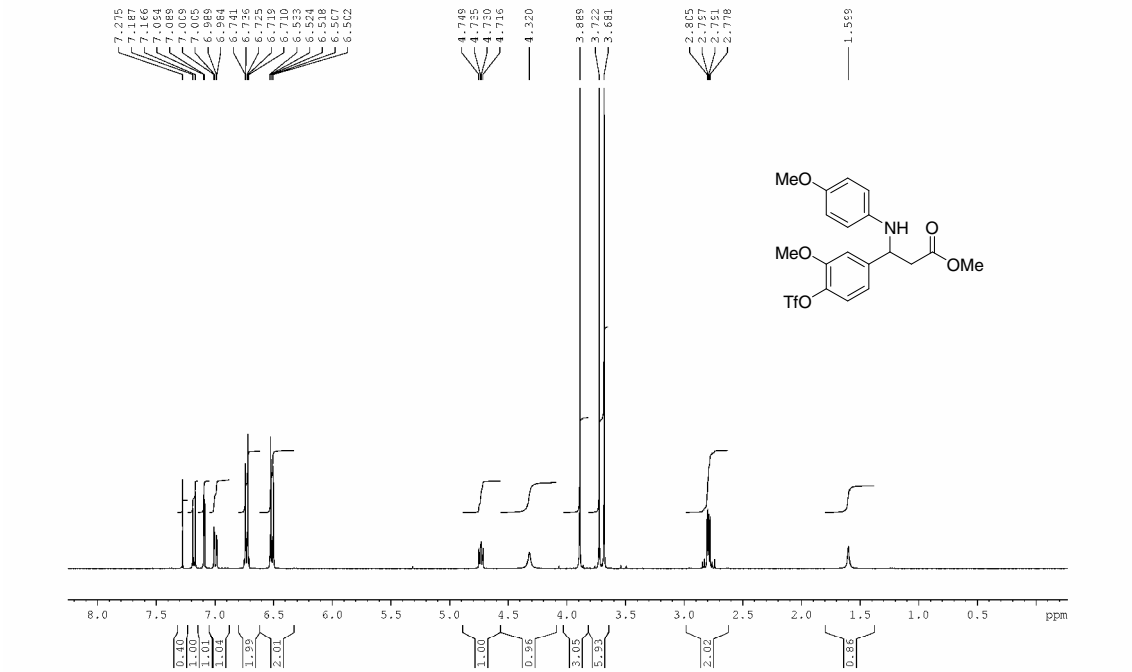

JS 145(42 46)
8.012
7.952
7.457
7.446
6.710
6.705
6.693
6.688
6.517
6.512
6.500
6.495
4.830
4.813
4.797
3.901
3.753
3.684
3.636
2.818
2.804
2.803
2.057
MeO
NH
O
OMe
MeO
O
ppm

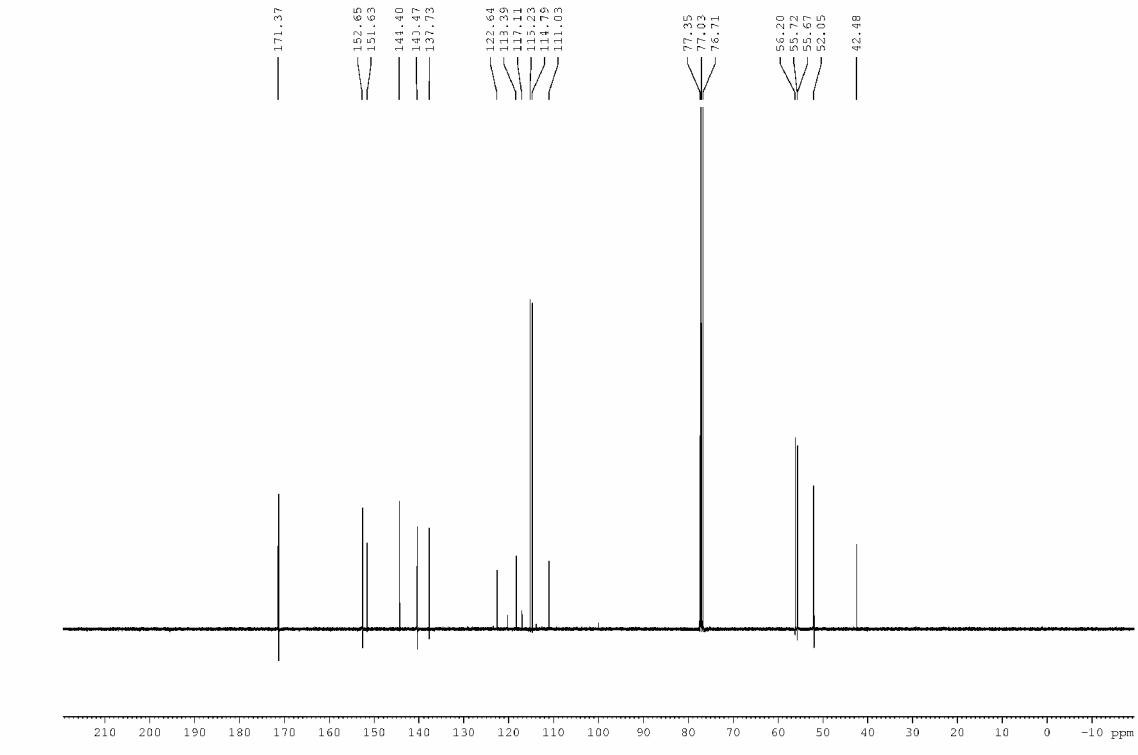

171.39
166.84
152.49
147.00
140.54
130.13
129.37
126.41
116.43
115.23
114.79
114.75
77.41
77.09
76.78
55.72
55.66
52.11
51.98
42.35
ppm


JS-162-24-31
MeO
NH
O
OMe
F
F
F
F
F
9.5
9.0
8.5
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
0.5
ppm
1.61
2.89
2.83
3.00
1.86
5.51
0.94
0.94
172.37
153.40
145.23
143.89
143.82
141.76
139.36
139.23
138.93
138.89
138.77
138.56
138.44
135.25
135.09
129.17
123.82
119.92
115.26
115.11
77.23
55.57
47.33
39.72
23.81
23.62
-0.00
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

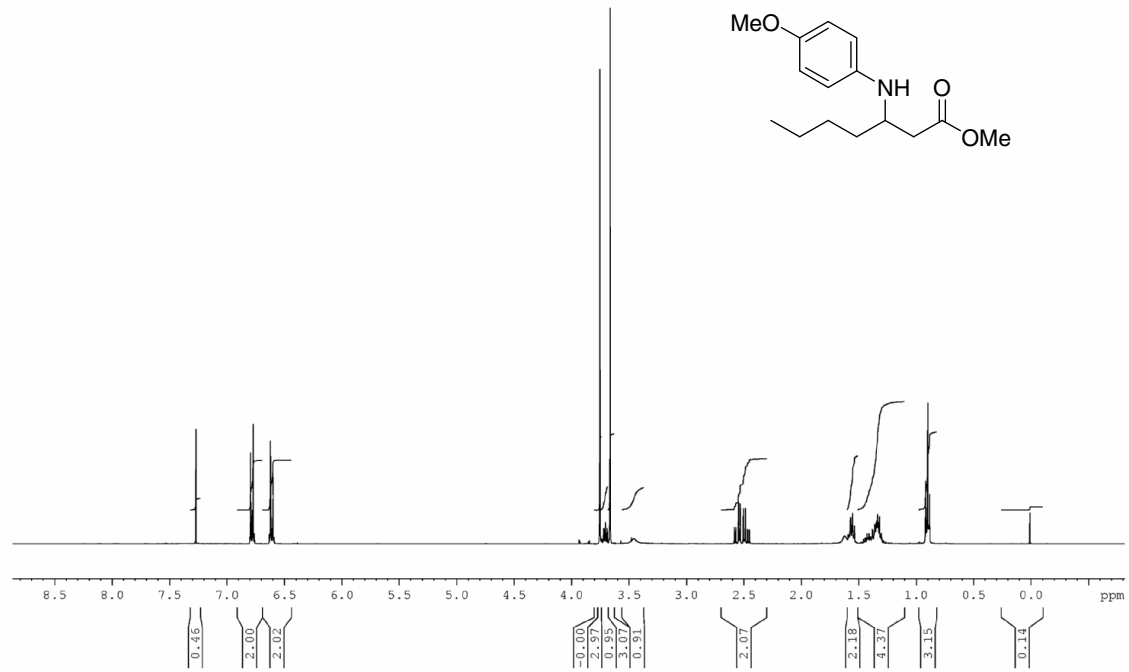

MeO
NH
O
EtO
OMe
O
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 ppm
1.85
1.84
1.00
1.95
5.82
1.93
2.83
0.15


172.53
171.08
153.20
143.16
115.91
114.84
77.37
77.26
77.06
76.74
61.60
55.68
55.02
52.02
37.38
14.12
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

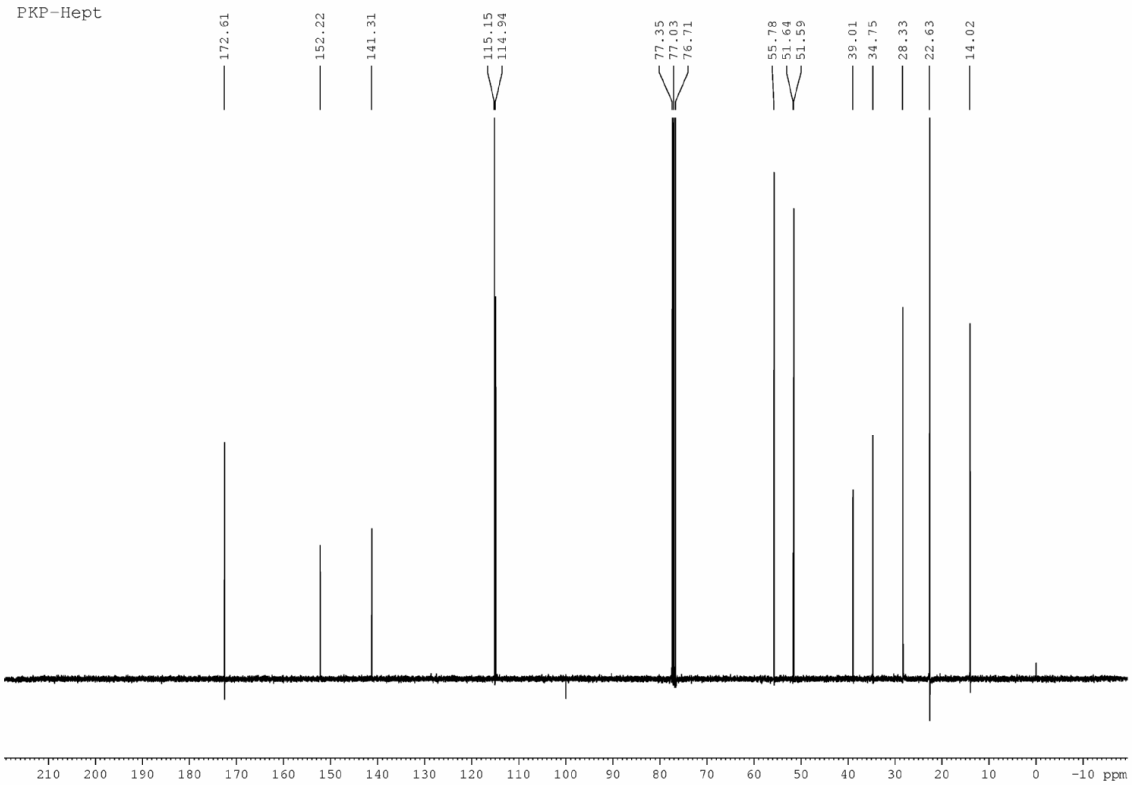

7.275
7.187
7.166
7.054
7.089
7.069
7.005
6.989
6.984
6.741
6.736
6.725
6.719
6.710
6.633
6.524
6.518
6.507
6.502
4.749
4.735
4.730
4.716
4.320
3.889
3.722
3.681
2.805
2.797
2.791
2.778
1.599
MeO
NH
O
MeO
OMe
TfO
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.40
1.00
1.01
1.04
1.99
2.01
1.00
0.96
3.05
5.93
2.02
0.86

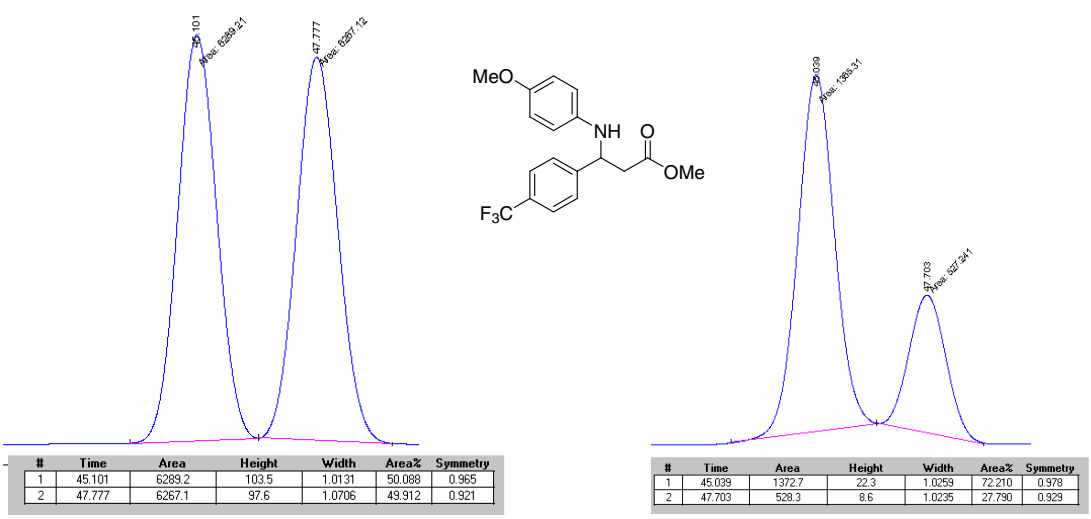

171.37
152.65
151.63
144.40
143.47
137.73
122.64
113.39
117.11
115.23
114.79
111.03
77.35
77.03
76.71
56.20
55.72
55.67
52.05
42.48
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10 ppm

PKP-Hept



PKP-Hept





#	Time	Area	Height	Width	Area%	Symmetry
1	45.101	6289.2	103.5	1.0131	50.088	0.965
2	47.777	6267.1	97.6	1.0706	49.912	0.921

#	Time	Area	Height	Width	Area%	Symmetry
1	45.039	1372.7	22.3	1.0259	72.210	0.978
2	47.703	528.3	8.6	1.0235	27.790	0.929

HPLC analysis using CHIRALCEL OD-RH column (45:55 CH_3CN-H_2O).