Electronic Supplementary Information (ESI)

A Powerful Synergistic Effect for Highly Efficient Diastereo- and Enantioselective Phase-Transfer Catalyzed Conjugate Additions

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Contents

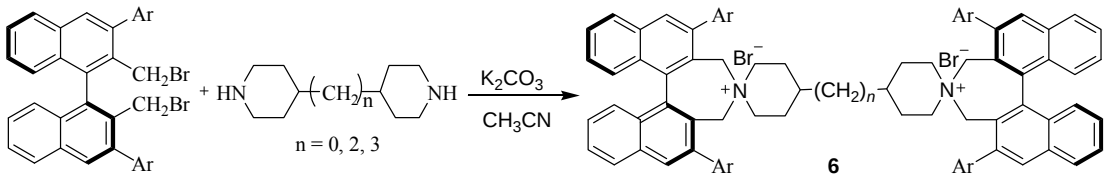
1. General information:

NMR spectra were recorded on Varian Mercury Plus 500 instruments at 500 MHz (^{1}H NMR), 125 MHz (^{13}C NMR) or Bruker AvanCE^{III} 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR). Chemical shifts were reported in ppm down field from internal Me_4Si. MS were recorded on a VG ZAB–HS spectrometer with the ESI resource. Optical rotations were determined using an Autopol IV–T. IR spectra were recorded on an AVATAR 360 FT–IR spectromer. HPLC analyses were carried out on a Hewlett Packard Model HP 1200 instrument.

Materials:

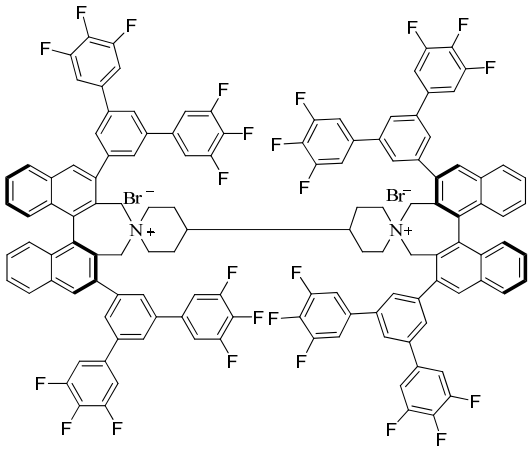
Tetrahydrofuran (THF), diethyl ether, benzene and toluene were distilled from sodium/benzophenone prior to use; CH_2Cl_2 were distilled from CaH_2. All purchased reagents were used without further purification. 4,4'-Bipiperidine dihydrochloride and 4,4'-Ethylenedipiperidine dihydrochloride were purchased from Aldrich chemicals, Inc. 1,3-Bis(4-piperidinyl)propane was purchased from Alfa Aesar chemicals, Inc. 3,3-disubstituted (*S*)-binol-derived were synthesized according to the literatures.[1]

2. Preparation of catalysts:



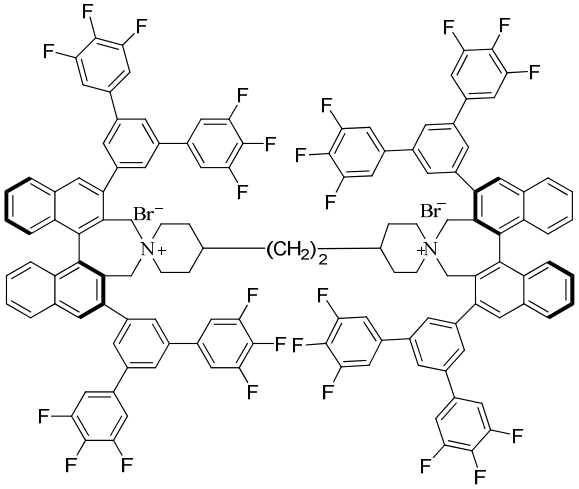
6a, *n* = 0, Ar = 3,5-(3,4,5-$F_3C_6H_2)_2C_6H_3$; **6b**, *n* = 2, Ar = 3,5-(3,4,5-$F_3C_6H_2)_2C_6H_3$
6c, *n* = 3, Ar = 3,5-(3,4,5-$F_3C_6H_2)_2C_6H_3$; **6d**, *n* = 0, Ar =3,5-[3,5-$(CF_3)_2C_6H_3]_2C_6H_3$
6e, *n* = 2, Ar = 3,5-[3,5-$(CF_3)_2C_6H_3]_2C_6H_3$; **6f**, *n* = 3, Ar = 3,5-[3,5-$(CF_3)_2C_6H_3]_2C_6H_3$

A mixture of 3,3-disubstituted (*S*)-binol-derived dibromide[1] (1.1 mmol), Bipiperidine (0.5 mmol) and K_2CO_3 (207 mg, 1.5 mmol) in acetonitrile (10 mL) was heated to reflux, and stirring was maintained for 48 h. The resulting mixture was poured into water and extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatographyon silica gel (MeOH/CH_2Cl_2 = 1/50 as eluant) to furnish (*S*,*S*)-**6**.

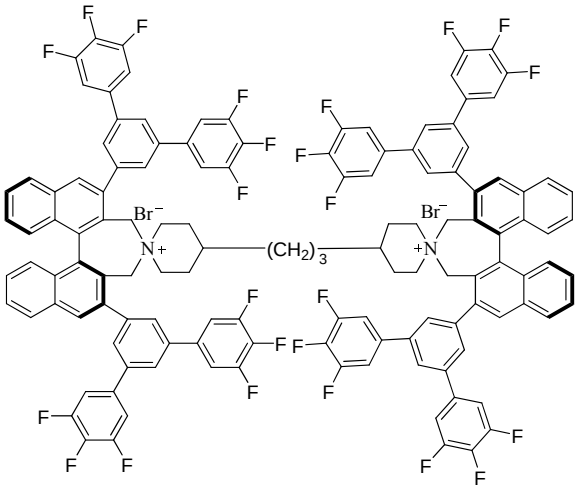


(*S*,*S*)-6a: 624.9 mg, 56% yield; $[\alpha]^{20}_D$ −9.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.76–0.78 (m, 2H), 1.06–1.07 (m, 2H), 1.13–1.16 (m, 2H), 1.24–1.26 (m, 4H), 2.77 (d, *J* = 10.5 Hz, 4H), 3.20–3.21 (m, 2H), 3.60–3.74 (m, 4H), 3.86 (d, *J* = 12.5 Hz, 2H), 4.45–4.48 (m, 2H), 5.36–5.39 (m, 2H), 7.29–7.32 (m, 8H), 7.42–7.49 (m, 20H), 7.68–7.73 (m, 8H), 7.90 (s, 4H), 8.08–8.12 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5–152.6 (m), 152.3–152.4 (m), 150.1–150.1 (m), 149.8–149.9 (m), 140.9–141.1 (m), 140.4–140.6 (m), 139.9–140.1 (m), 139.5–139.6 (m), 138.9, 138.4, 138.3, 138.1, 138.0, 137.8, 136.3–136.8 (m), 135.2–135.3 (m), 134.5, 133.9, 133.6, 131.5, 130.9, 130.7, 130.5, 129.7, 129.0, 128.7, 128.5, 128.2, 127.9, 127.9, 127.6,

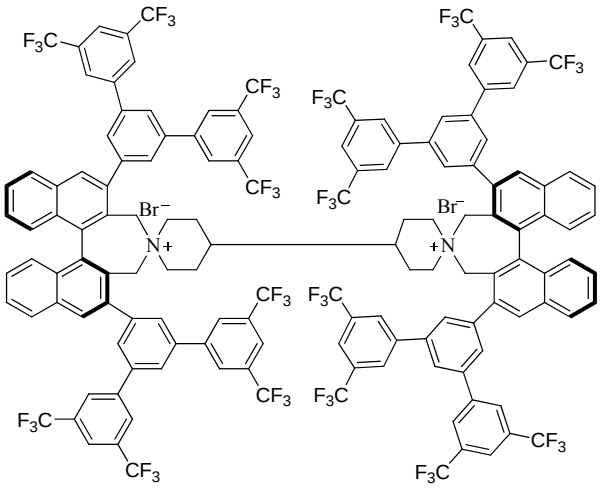
126.4, 126.3, 124.1, 123.5, 67.1, 62.8, 60.4, 58.1, 53.4, 52.5, 40.8, 34.4, 31.9, 29.7, 29.6, 29.3, 22.7, 21.0, 20.6, 18.3, 14.1; IR (KBr) ν 3398, 3053, 2934, 2858, 1616, 1585, 1526, 1456, 1400, 1345, 1242, 1044, 881, 852, 751, 663 cm^{-1}; MS (ESI) m/z 1035.63 ($[M - 2Br]^{2+}/2$, $C_{126}H_{74}F_{24}N_2^{2+}$ requires 1035.95).



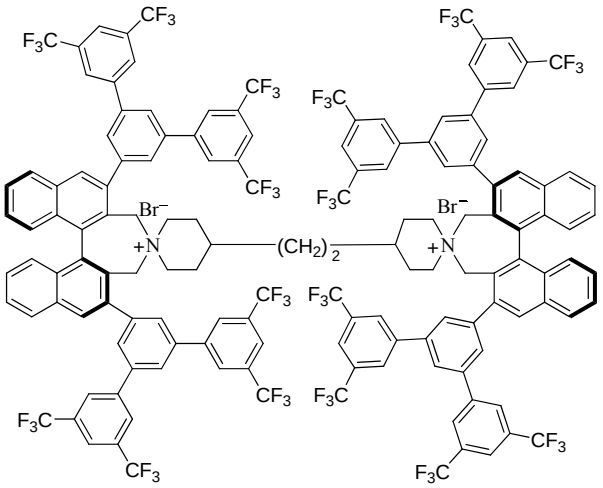
(*S*,*S*)-6b: 564.9 mg, 50% yield; $[\alpha]^{20}_D$ +5.5 (*c* 1.0, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) δ 0.70–0.72 (m, 2H), 0.84–0.92 (m, 4H), 1.12–1.26 (m, 8H), 2.59–2.65 (m, 2H), 2.93–3.09 (m, 4H), 3.49–3.59 (m, 2H), 3.77–3.90 (m, 4H), 4.90–5.01 (m, 4H), 7.14–7.17 (m, 2H), 7.22–7.24 (m, 2H), 7.33 (t, *J* = 6.5 Hz, 6H), 7.41–7.52 (m, 20H), 7.69–7.77 (m, 10H), 8.03 (d, *J* = 7.5 Hz, 2H), 8.09 (d, *J* = 8.0 Hz, 2H), 8.18 (d, *J* = 9.5 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$ & CD_3OD) δ 152.6–152.7 (m), 152.4–152.5 (m), 150.6–150.7 (m), 150.4–150.5 (m), 141.3–141.4 (m), 140.7–140.8 (m), 140.6–140.7 (m), 140.4–140.5 (m), 139.9, 139.5, 138.8, 138.6, 138.1, 137.8, 136.5–136.7 (m), 135.9–136.1 (m), 134.2, 131.7, 131.2, 131.1, 131.0, 129.1, 129.0, 128.9, 128.7, 128.6, 128.5, 128.2, 128.1, 128.0, 128.0, 127.8, 127.6, 127.6, 126.0, 125.3, 123.9, 123.5, 63.0, 60.3, 57.4, 56.5, 53.6, 52.4, 32.0, 31.8, 30.1, 29.7, 29.7, 29.4, 26.5, 25.7, 22.7, 21.0, 17.6, 13.8; IR (KBr) ν 3324, 3049, 2929, 2863, 1616, 1527, 1457, 1400, 1345, 1243, 1044, 852, 748, 664 cm^{-1}; MS (ESI) m/z 1049.73 ($[M - 2Br]^{2+}/2$, $C_{128}H_{78}F_{24}N_2^{2+}$ requires 1049.98).



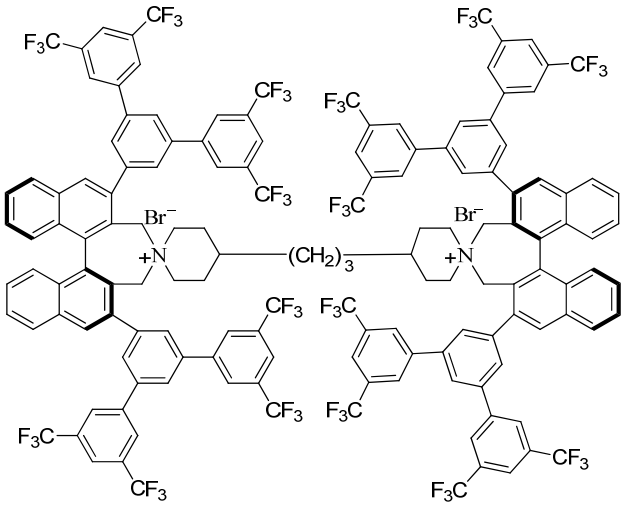
(*S*,*S*)-6c: 670.7 mg, 59% yield; $[\alpha]^{20}_{D}$ +3.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.52–0.55 (m, 2H), 0.67–0.69 (m, 2H), 0.84–0.89 (m, 4H), 1.25 (s, 4H), 1.41 (d, *J* = 11.0 Hz, 4H), 2.79 (d, *J* = 11.0 Hz, 2H), 3.17 (s, 4H), 3.49 (d, *J* = 13.0 Hz, 2H), 3.84–3.89 (m, 4H), 4.96 (t, *J* = 14.5 Hz, 4H), 7.25–7.28 (m, 2H), 7.31–7.49 (m, 24H), 7.54 (s, 2H), 7.62–7.70 (m, 8H), 7.77 (s, 2H), 7.83 (s, 2H), 8.06–8.10 (m, 4H), 8.15 (s, 2H), 8.20 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4–152.6 (m), 152.2–152.3 (m), 150.4–150.6 (m), 150.2–150.3 (m), 141.3–141.4 (m), 140.7–140.9 (m), 140.4–140.6 (m), 139.9–140.1 (m), 139.6, 138.9, 138.6, 138.5, 138.0, 136.4–136.5 (m), 135.7–135.8 (m), 134.1, 133.2, 131.9, 131.8, 131.8, 131.3, 131.2, 131.0, 129.4, 129.3, 129.2, 129.2, 128.9, 128.8, 128.6, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 125.9, 125.3, 124.0, 123.7, 63.0, 60.3, 57.9, 57.1, 53.8, 52.8, 35.5, 33.9, 33.5, 32.1, 30.7, 29.9, 29.8, 29.5, 26.5, 26.0, 25.6, 25.0, 22.9, 18.4, 14.3; IR (KBr) ν 3395, 3052, 2930, 2858, 1616, 1585, 1532, 1456, 1400, 1345, 1243, 1041, 852, 789, 664 cm^{-1}; MS (ESI) m/z 1056.99 ($[M - 2Br]^{2+}/2$, $C_{129}H_{80}F_{24}N_2^{2+}$ requires 1056.99).



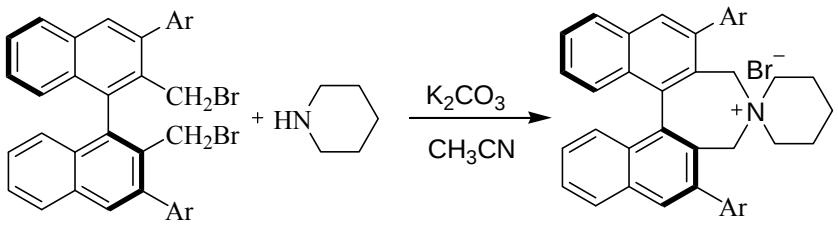
(*S*,*S*)-6d: 837.5 mg, 58% yield; $[\alpha]^{20}_{D}$ −18.0 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95–0.97 (m, 2H), 1.28 (s, 8H), 2.30–2.36 (m, 2H), 2.87 (s, 4H), 3.24 (d, *J* = 10.5 Hz, 2H), 3.90–4.13 (m, 4H), 4.55–4.57 (m, 2H), 5.49–5.49 (m, 2H), 7.42 (s, 2H), 7.49–7.53 (m, 10H), 7.57–7.59 (m, 3H), 7.70–7.73 (m, 7H), 7.77–7.79 (m, 6H), 7.88–7.93 (m, 6H), 8.10–8.17 (m, 10H), 8.20–8.25 (m, 8H), 8.43 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.6, 142.6, 142.5, 141.4, 141.4, 141.2, 141.0, 140.3, 140.1, 139.8, 139.2, 138.7, 138.1, 134.1, 133.9, 132.5, 132.3, 132.2, 132.1, 132.0, 131.9, 131.8, 131.7, 131.7, 131.6, 131.5, 131.3, 131.1, 131.0, 130.8, 130.7, 130.0, 129.5–125.7 (m), 129.2, 129.1–129.2 (m), 129.0, 128.9, 128.8, 128.7, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.5, 127.0, 126.7, 125.5, 124.8, 124.6, 124.5, 124.3, 123.9, 122.6, 122.4, 122.4, 121.6, 121.5, 121.1, 120.5, 120.2, 60.6, 58.2, 55.3, 53.6, 33.6, 32.2, 30.5, 29.9, 29.9, 29.6, 24.7, 23.0, 22.9, 21.6, 18.4, 14.3; IR (KBr) ν 3349, 3067, 2926, 2863, 1618, 1588, 1464, 1368, 1279, 1178, 1136, 899, 844, 707, 683 cm^{-1}; MS (ESI) m/z 1363.66 ($[M - 2Br]^{2+}/2$, $C_{142}H_{82}F_{48}N_2^{2+}$ requires 1364.05).



(*S*,*S*)-6e: 903.9 mg, 62% yield; $[\alpha]^{20}_{D}$ –2.1 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.62 (s, 4H), 0.97–0.99 (m, 2H), 1.25 (d, *J* = 11.5 Hz, 8H), 2.73 (d, *J* = 11.5 Hz, 2H), 3.14 (s, 4H), 3.30–3.36 (m, 2H), 3.60 (d, *J* = 13.0 Hz, 2H), 3.83 (d, *J* = 13.0 Hz, 2H), 4.67 (d, *J* = 8.5 Hz, 2H), 5.01 (d, *J* = 12.5 Hz, 2H), 7.50–7.54 (m, 10H), 7.74–7.79 (m, 10H), 7.85 (d, *J* = 14.5 Hz, 4H), 7.91–7.94 (m, 8H), 8.02 (s, 4H), 8.08 (d, *J* = 5.5 Hz, 8H), 8.14 (s, 6H), 8.20–8.23 (m, 4H), 8.36 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$ & CD_3OD) δ 146.5, 146.4, 145.9, 145.7, 144.7, 144.7, 144.6, 143.1, 143.0, 142.0, 142.0, 138.2, 138.1, 137.2, 137.1, 136.9, 136.8, 136.7, 136.6, 136.5, 136.4, 136.3, 136.2, 136.1, 135.9, 135.9, 135.6–135.8 (m), 135.3–135.4 (m), 135.2, 135.1, 133.5–133.7 (m), 133.0–133.1 (m), 132.9, 132.4, 132.2, 131.9, 131.7, 131.6, 131.4, 131.1, 130.6, 130.5, 130.4, 130.0, 128.5, 128.4, 128.3., 128.2, 127.4, 127.3, 126.3–126.4 (m), 126.3, 126.2, 126.1, 126.0, 125.5–125.6 (m), 124.1, 124.0. 123.9. 123.9. 72.2, 71.7, 66.9, 64.1, 63.8, 59.8, 56.3, 36.0, 34.6, 33.7, 33.4, 31.4, 30.2, 30.2, 29.7, 26.7, 22.6, 18.8, 18.0; IR (KBr) ν 3349, 3047, 2929, 2858, 1618, 1588, 1464, 1368, 1279, 1170, 1136, 882, 844, 707, 683 cm^{-1}; MS (ESI) m/z 1378.07 ([M – 2Br]$^{2+}$/2, $C_{144}H_{86}F_{48}N_2^{2+}$ requires 1378.08).



(*S*,*S*)-6f: 937.6 mg, 64% yield; $[\alpha]^{20}_{D}$ +4.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.47–0.49 (m, 2H), 0.66–0.68 (m, 2H), 0.78–0.80 (m, 2H), 0.84–0.94 (m, 2H), 1.14 (s, 2H), 1.26 (s, 2H), 1.36 (s, 2H), 1.48 (d, *J* = 13.0 Hz, 2H), 2.96–3.02 (m, 4H), 3.23 (d, *J* = 11.0 Hz, 2H), 3.45 (t, *J* = 11.5 Hz, 2H), 3.60–3.64 (m, 2H), 4.03 (d, *J* = 13.5 Hz, 2H), 4.79 (d, *J* = 13.0 Hz, 2H), 5.07 (d, *J* = 13.0 Hz, 2H), 7.49–7.57 (m, 8H), 7.61 (s, 2H), 7.72–7.76 (m, 4H), 7.86 (t, *J* = 10.0 Hz, 8H), 7.95 (d, *J* = 12.0 Hz, 6H), 7.99 (s, 2H), 8.05 (s, 6H), 8.17 (d, *J* = 7.5 Hz, 8H), 8.21 (d, *J* = 13.0 Hz, 8H), 8.27 (s, 2H), 8.31 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$ & CD_3OD) δ 142.4 ,142.0, 141.9, 141.9, 141.8, 141.2, 141.0, 140.6, 140.5, 139.3, 139.0, 138.2, 138.2, 134.3, 134.2, 133.2, 130.0, 132.9, 132.7, 132.6, 132.5, 132.4–132.5 (m), 132.2–132.3 (m), 132.1, 131.9–132.0 (m), 131.7, 131.3, 131.1, 130.6, 130.2, 130.0–130.1 (m), 129.9, 129.2, 129.1, 129.0, 129.0, 128.9, 128.9, 128.6, 128.3, 128.2, 128.2, 128.0, 127.8 127.7, 127.6, 126.9, 126.7, 126.6, 126.5, 126.2, 125.4, 124.6, 124.5, 124.3, 123.7, 123.4, 122.4, 122.3, 122.2–122.3 (m), 122.2, 121.7–121.8 (m), 120.2, 120.1, 120.0, 63.1, 60.3, 57.7, 56.8, 53.7, 52.6, 35.5, 32.0, 30.9, 29.8, 29.8, 29.5, 26.9, 25.5, 22.8, 22.6, 20.8, 17.9, 14.1; IR (KBr) ν 3339, 3057, 2934, 2893, 1623, 1598, 1460, 1368, 1279, 1176, 1132, 883, 844, 702, 684 cm^{-1}; MS (ESI) m/z 1385.07 ($[M - 2Br]^{2+}/2$, $C_{145}H_{88}F_{48}N_2^{2+}$ requires 1385.09).



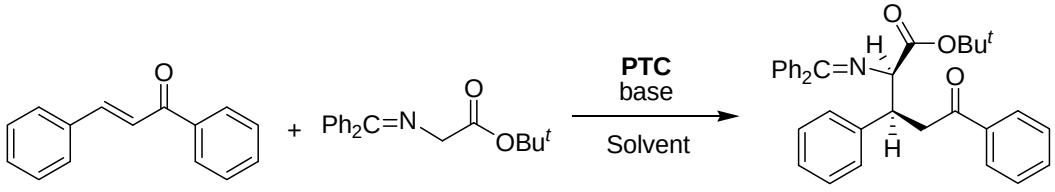
8

Ar = 3,5-[3,5-$(CF_3)_2C_6H_3]_2C_6H_3$

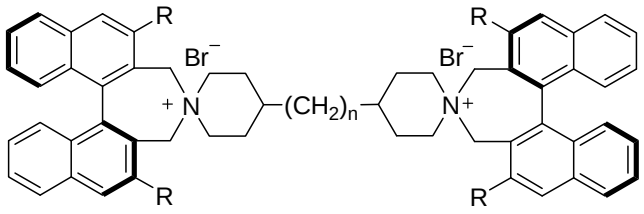
A mixture of 3,3-disubstituted (*S*)-binol-derived dibromide[1] (792.5 mg, 0.55 mmol), piperidine (42.6 mg, 0.5 mmol) and K_2CO_3 (103.7 mg, 0.75 mmol) in acetonitrile (5 mL) was heated to reflux, and stirring was maintained for 12 h. The resulting mixture was poured into water and extracted with CH_2Cl_2. The organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatographyon silica gel (MeOH/CH_2Cl_2 = 1/30 as eluant) to furnish (*S*)-**8**.

(*S*)-8: 540.5 mg, 75% yield. $[\alpha]^{20}_D$ –0.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87–0.95 (m, 2H), 1.36–1.45 (m, 2H), 1.57 (s, 2H), 3.35 (s, 2H), 3.75 (d, *J* = 13.2 Hz, 2H), 3.95 (s, 2H), 5.37 (d, *J* = 13.2 Hz, 2H), 7.49–7.57 (m, 4H), 7.67 (s, 2H), 7.74 (t, *J* = 7.2 Hz, 2H), 7.88 (d, *J* = 7.2 Hz, 4H), 7.94 (d, *J* = 8.8 Hz, 4H), 8.14–8.23 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 141.8, 141.2, 141.0, 140.8, 138.9, 138.4, 133.9, 133.1, 132.7, 132.4, 132.1, 131.7, 131.6, 131.4–131.5 (m), 130.9, 129.6, 128.8, 128.5, 128.1, 127.5, 127.3, 126.7, 124.6, 123.7, 121.9–122.0 (m), 121.8, 119.1, 60.3, 58.1, 58.0, 57.8, 29.7, 20.3, 19.7; IR (KBr) ν 3666, 3349, 3062, 2939, 1618, 1587, 1500, 1469, 1368, 1280, 1175, 1129, 1024, 885, 844, 742, 706 cm^{-1}; MS (ESI) m/z 1364.52 ($[M - Br]^+$, $C_{71}H_{42}F_{24}N^+$ requires 1365.06).

3. Optimizing of the Michael Addition Conditions:[a]



PTC



Cat-1, n = 0, R = H; **Cat-2**, n = 2, R = H; **Cat-3**, n = 3, R = H;
Cat-4, n = 0, R = C_6H_5; **Cat-5**, n = 2, R = C_6H_5; **Cat-6**, n = 3, R = C_6H_5;
Cat-7, n = 0, R = 3,4,5-$F_3C_6H_2$; **Cat-8**, n = 2, R = 3,4,5-$F_3C_6H_2$;
Cat-9, n = 3, R = 3,4,5-$F_3C_6H_2$; **7a**, n = 0, R = 3,5-$(CF_3)_2C_6H_3$;
Cat-10, n = 2, R = 3,5-$(CF_3)_2C_6H_3$; **7b**, n = 3, R = 3,5-$(CF_3)_2C_6H_3$.

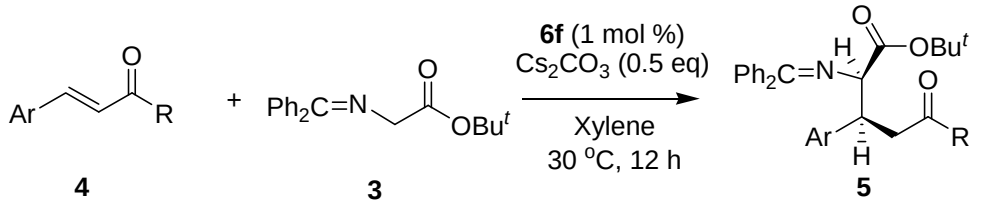
6a, *n* = 0, Ar = 3,5-(3,4,5-$F_3C_6H_2)_2C_6H_3$; **6b**, *n* = 2, Ar = 3,5-(3,4,5-$F_3C_6H_2)_2C_6H_3$
6c, *n* = 3, Ar = 3,5-(3,4,5-$F_3C_6H_2)_2C_6H_3$; **6d**, *n* = 0, Ar =3,5-[3,5-$(CF_3)_2C_6H_3]_2C_6H_3$
6e, *n* = 2, Ar = 3,5-[3,5-$(CF_3)_2C_6H_3]_2C_6H_3$; **6f**, *n* = 3, Ar = 3,5-[3,5-$(CF_3)_2C_6H_3]_2C_6H_3$

entry	Catalyst (mol %)	temp (^oC)	solvent	base	time (h)	yield (%) [f]	er [g]	dr [h]
1	**Cat-1** (2)	10	toluene	Cs_2CO_3(2eq)	36	85	56.5:43.5	97:3
2	**Cat-2** (2)	10	toluene	Cs_2CO_3(2eq)	36	87	56.5:43.5	97:3
3	**Cat-3** (2)	10	toluene	Cs_2CO_3(2eq)	36	84	54.5:45.5	97:3
4	**Cat-4** (1)	10	toluene	Cs_2CO_3(2eq)	48	95	66.5:33.5	97:3
5	**Cat-5** (1)	10	toluene	Cs_2CO_3(2eq)	48	98	72:28	95:5
6	**Cat-6** (1)	10	toluene	Cs_2CO_3(2eq)	48	92	61.5:38.5	97:3
7	**Cat-7** (1)	10	toluene	Cs_2CO_3(2eq)	48	86	65:35	95:5
8	**Cat-8** (1)	10	toluene	Cs_2CO_3(2eq)	48	92	72.5:27.5	96:4
9	**Cat-9** (1)	10	toluene	Cs_2CO_3(2eq)	48	92	75:25	96:4
10	**7a** (1)	10	toluene	Cs_2CO_3(2eq)	48	98	74.5:25.5	98:2
11	**Cat-10** (1)	10	toluene	Cs_2CO_3(2eq)	48	90	74:26	98:2
12	**7b** (1)	10	toluene	Cs_2CO_3(2eq)	48	85	72.5:27.5	97:3
13	**6a** (1)	10	toluene	Cs_2CO_3(0.5eq)	48	88	69:31	97:3
14	**6b** (1)	10	toluene	Cs_2CO_3(0.5eq)	48	98	90:10	97:3
15	**6c** (1)	10	toluene	Cs_2CO_3(0.5eq)	48	98	85:15	97:3
16	**6d** (1)	10	toluene	Cs_2CO_3(0.5eq)	48	95	86.5:13.5	97:3
17	**6e** (1)	10	toluene	Cs_2CO_3(0.5eq)	48	96	83.5:16.5	97:3
18	**6f** (1)	10	toluene	Cs_2CO_3(0.5eq)	48	98	94:6	96:4
19	**6f** (1)	10	xylene	Cs_2CO_3(0.5eq)	48	98	95:5	98:2
20	**6f** (1)	10	CH_2Cl_2	Cs_2CO_3(0.5eq)	48	96	70:30	96:4

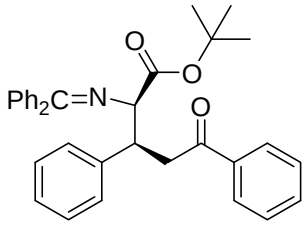
21	**6f** (1)	10	THF	Cs_2CO_3(0.5eq)	48	90	79.5:20.5	96:4
22	**6f** (1)	10	Et_2O	Cs_2CO_3(0.5eq)	48	93	91:9	98:2
23	**6f** (1)	10	benzene	Cs_2CO_3(0.5eq)	48	98	86:14	97:3
24	**6f** (1)	10	chlorobenzene	Cs_2CO_3(0.5eq)	48	98	83:17	97:3
25	**6f** (1)	10	fluorobenzene	Cs_2CO_3(0.5eq)	48	98	93:7	97:3
26 [b]	**6f** (1)	10	toluene	Cs_2CO_3(0.5eq)	48	92	92:8	97:3
27	**6f** (1)	10	anisole	Cs_2CO_3(0.5eq)	48	96	85:15	97:3
28	**6f** (1)	10	mesitylene	Cs_2CO_3(0.5eq)	48	94	85:15	97:3
29	**6f** (1)	10	*p*-xylene	Cs_2CO_3(0.5eq)	48	93	85:15	97:3
30	**6f** (1)	10	*m*-xylene	Cs_2CO_3(0.5eq)	48	97	81.5:18.5	96:4
31	**6f** (1)	10	*o*-xylene	Cs_2CO_3(0.5eq)	48	95	81:19	97:3
32 [c]	**6f** (1)	10	xylene	Cs_2CO_3(0.5eq)	48	98	92:8	97:3
33 [d]	**6f** (1)	10	xylene	Cs_2CO_3(0.5eq)	48	98	89.5:10.5	97:3
34	**6f** (0.5)	10	xylene	Cs_2CO_3(0.5eq)	60	98	85:15	97:3
35 [e]	**6f** (1)	10	xylene	Cs_2CO_3(0.5eq)	72	82	94:6	98:2
36	**6f** (1)	10	xylene	K_2CO_3(2eq)	72	72	96.5:3.5	96:4
37	**6f** (1)	10	xylene	CsOH(1eq)	40	63	50:50	86:14
38	**6f** (1)	10	xylene	NaOH(1eq)	36	96	50:50	82:18
39	**6f** (1)	10	xylene	Na_2CO_3(2eq)	48	<5	\	\
40	**6f** (2)	10	xylene	Cs_2CO_3(0.5eq)	36	96	95:5	97:3
41	**6f** (2)	10	xylene	K_2CO_3(2eq)	72	83	96:4	95:5
42	**6f** (1)	10	xylene	Cs_2CO_3(0.2eq)	48	89	95:5	97:3
43	**6f** (1)	10	xylene	Cs_2CO_3(0.1eq)	48	69	95:5	96:4
44	**6f** (1)	10	xylene	Cs_2CO_3(0.05eq)	48	85	95:5	97:3
45	**6f** (1)	0	xylene	Cs_2CO_3(0.5eq)	96	72	91:9	98:2
46	**6f** (1)	25	xylene	Cs_2CO_3(0.5eq)	24	98	95.5:4.5	97:3
47	**6f** (1)	**30**	**xylene**	**Cs_2CO_3(0.5eq)**	**12**	**98**	**96.5:3.5**	**97:3**
48	**6f** (1)	35	xylene	Cs_2CO_3(0.5eq)	12	98	95:5	95:5
49	**6f** (1)	40	xylene	Cs_2CO_3(0.5eq)	12	98	92.5:7.5	93:7
50	**6f** (1)	30	xylene	K_2CO_3(2eq)	12	78	96:4	97:3

[a] *N*-(diphenylmethylene)glycine *tert*-butyl ester **3** (29.5 mg, 0.1 mmol), chalcone **4a** (21.8 mg, 0.105 mmol), **PTC**, base, 0.5mL solvent. [b] Toluene was used without further purification. [c] Xylene was distilled from CaH_2. [d] 0.25 mL xylene and 0.25 ml hexane. [e] 1 mL xylene. [f] Yield of isolated product after purification. [g] Determined by HPLC analysis. [h] Determined by NMR or HPLC.

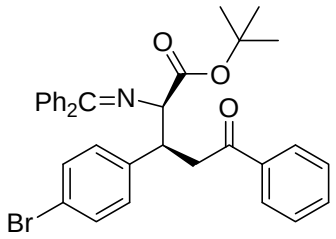
4. General Procedure for Catalyzed Michael Addition:



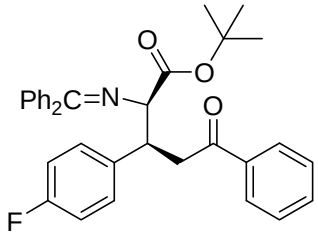
N-(diphenylmethylene)glycine *tert*-butyl ester **3** (29.5 mg, 0.1 mmol) was added to a mixture of substituted enones **4** (0.105 mmol), (*S*,*S*)-**6f** (2.9 mg, 0.001 mmol) and Cs_2CO_3 (16.3 mg, 0.05 mmol) in xylene (0.5 mL) under argon atmosphere, the resulting solution was stirred at 30 °C for 12 h. The resulting mixture was purified by column chromatographyon silica gel (AcOEt/petroleum ether = 1/10 as eluant) to furnish the conjugate adducts **5**.



(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-oxo-3,5-diphenylpentanoate (5a): 49.4 mg, 98% yield; $[\alpha]^{20}_{D}$ +81.7 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (s, 9H), 3.64–3.67 (m, 1H), 3.77–3.83 (m, 1H), 4.22–4.26 (m, 2H), 6.75 (d, *J* = 6.5 Hz, 1H), 7.14–7.19 (m, 5H), 7.32–7.39 (m, 5H), 7.42–7.47 (m, 3H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.9, 171.4, 170.2, 141.6, 139.6, 137.4, 136.5, 133.1, 130.6, 129.1, 128.8, 128.7, 128.6, 128.5, 128.4, 128.4, 128.3, 127.7, 126.8, 84.5, 71.2, 45.0, 40.3, 28.1; MS (ESI) m/z 504.14 $[M + 1]^+$; IR (KBr) ν 3060, 3021, 2976, 2930, 1728, 1687, 1622, 1597, 1493, 1447, 1367, 1286, 1148, 1002, 846, 698 cm^{-1}; *dr* = 97/3, *er* = 96.5/3.5, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 95/5, 0.5 ml/min, 254 nm UV detector), t_R = 21.8 min (major) and t_R = 30.3 min (minor).

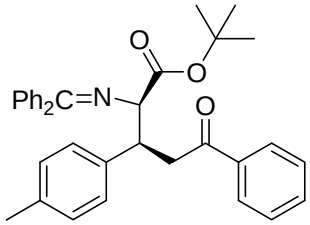


(2*R*,3*S*)-*tert*-Butyl 3-(4-bromophenyl)-2-(diphenylmethyleneamino)-5-oxo-5-phenylpentanoate (5b): 57.1 mg, 98% yield; $[\alpha]^{20}_{D}$ +52.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (s, 9H), 3.60–3.63 (m, 1H), 3.75–3.81 (m, 1H), 4.15–4.18 (m, 2H), 6.75 (d, *J* = 6.0 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 7.29–7.39 (m, 7H), 7.41–7.48 (m, 3H), 7.54–7.57 (m, 1H), 7.67–7.69 (m, 2H), 7.97–7.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 171.7, 170.0, 140.8, 139.4, 137.2, 136.3, 133.2, 131.4, 130.7, 130.5, 129.0. 128.8, 128.7, 128.5, 128.4, 128.3, 127.6, 120.6, 81.8, 70.8, 44.3, 39.9, 29.1; MS (ESI) m/z 584.11 $[M + 1]^+$, 582.13 $[M + 1]^+$; IR (KBr) ν 3058, 2974, 2931, 1730, 1686, 1621, 1596, 1488, 1447, 1368, 1285, 1149, 1074, 1010, 834, 698 cm^{-1}; *dr* = 95/5, *er* = 94/6, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 95/5, 0.6 ml/min, 254 nm UV detector), t_R = 24.0 min (major) and t_R = 37.5 min (minor).

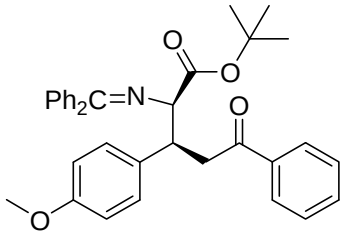


(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-3-(4-fluorophenyl)-5-oxo-5-phenylpentanoate (5c): 51.2 mg, 98% yield; $[\alpha]^{20}_{D}$ +74.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 9H), 3.59–3.63 (m, 1H), 3.70–3.75 (m, 1H), 4.16–4.22 (m, 2H), 6.78 (d, *J* = 6.5 Hz, 2H), 6.85–6.89(m, 2H), 7.12–7.15 (m, 2H), 7.34–7.39 (m, 5H), 7.41–7.47 (m, 3H), 7.53–7.56 (m, 1H), 7.69–7.71 (m, 2H), 7.96–7.98 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 171.6, 170.1, 162.8, 160.8, 139.4, 137.3, 137.3, 137.2, 136.4, 133.2, 130.7, 130.3, 130.2, 129.1, 128.8, 128.7, 128.5, 128.4, 128.3, 127.7, 115.7, 115.2, 81.7, 71.1, 44.2, 40.3, 28.1; MS (ESI) m/z 520.17 $[M – H]^–$; IR (KBr) ν 3062, 3010, 2975, 2928, 1733, 1674, 1621, 1596, 1510, 1446, 1365,

1288, 1220, 1157, 1011, 840, 692 cm^{-1}; *dr* = 96/4, *er* = 95/5, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 6.5 min (major) and t_R = 14.2 min (minor).

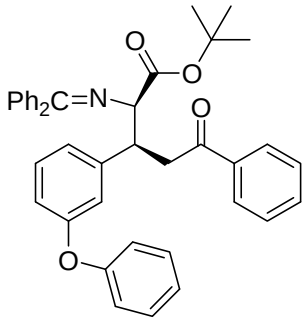


(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-oxo-5-phenyl-3-p-tolyl-pentanoate (5d): 50.8 mg, 98% yield; $[\alpha]^{20}_D$ +73.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (s, 9H), 2.27 (s, 3H), 3.63–3.66 (m, 1H), 3.75–3.80 (m, 1H), 4.17–4.21 (m, 2H), 6.77 (d, *J* = 7.0 Hz, 2H), 6.78 (d, *J* = 7.5 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.33–7.39 (m, 5H), 7.42–7.47 (m, 3H), 7.53–7.56 (m, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.0, 171.3, 170.3, 139.7, 138.5, 137.4, 136.6, 136.2, 133.0, 130.6, 129.1, 129.0, 128.7, 128.6, 128.6, 128.4, 128.3, 127.8, 81.4, 71.3, 44.7, 40.3, 28.1, 21.3; MS (ESI) m/z 518.23 $[M + 1]^+$; IR (KBr) ν 3062, 3027, 2970, 2924, 1728, 1687, 1629, 1598, 1511, 1447, 1367, 1289, 1149, 1003, 850, 695 cm^{-1}; *dr* = 95/5, *er* = 94/6, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 98/2, 0.8 ml/min, 254 nm UV detector), t_R = 8.5 min (major) and t_R = 24.8 min (minor).

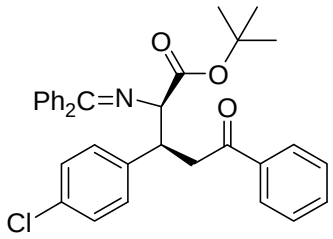


(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-3-(4-methoxyphenyl)-5-oxo-5-phenylpentanoate (5e): 49.1 mg, 92% yield; $[\alpha]^{20}_D$ +80.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 9H), 3.57–3.60 (m, 1H), 3.66–3.70 (m, 1H), 3.73 (s, 3H), 4.14–4.16 (m, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 7.0 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 7.33–7.38 (m, 5H), 7.40–7.46 (m, 3H), 7.52–7.55 (m, 1H), 7.70 (d, *J* = 7.5

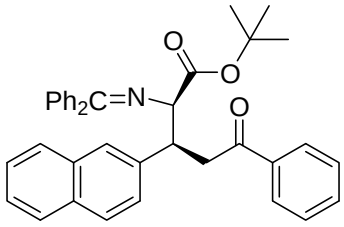
Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.1, 171.3, 170.3, 158.4, 139.6, 137.4, 136.5, 133.6, 133.0, 130.6, 129.7, 129.1, 128.7, 128.6, 128.5, 128.4, 128.2, 127.8, 113.7, 81.5, 71.3, 55.4, 44.3, 40.6, 28.1; MS (ESI) m/z 534.19 $[M + 1]^+$; IR (KBr) ν 3058, 3027, 2974, 2931, 1726, 1687, 1612, 1597, 1513, 1447, 1367, 1246, 1149, 1031, 830, 694 cm^{-1}; *dr* = 97/3, *er* = 96/4, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 8.7 min (major) and t_R = 24.4 min (minor).



(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-oxo-3-(3-phenoxyphenyl)-5-phenylpentanoate (5f): 58.4 mg, 98% yield; $[\alpha]^{20}_D$ +70.9 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (s, 9H), 3.55–3.59 (m, 1H), 3.72–3.78 (m, 1H), 4.13–4.18 (m, 2H), 6.79 (d, *J* = 7.5 Hz, 3H), 6.83 (d, *J* = 8.5 Hz, 3H), 6.93 (d, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 7.0 Hz, 1H), 7.13–7.21 (m, 3H), 7.33–7.41 (m, 6H), 7.44–7.47 (m, 2H), 7.54–7.57 (m, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.97 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 171.5, 170.1, 157.3, 157.1, 143.7, 139.5, 137.4, 136.5, 133.1, 130.6, 129.8, 129.6, 129.1 ,127.7, 128.6, 128.5, 128.4, 128.2, 127.7, 123.8, 123.1, 119.2, 118.8, 117.3, 81.6, 70.9, 44.8, 40.0, 28.1; MS (ESI) m/z 596.25 $[M + 1]^+$; IR (KBr) ν 3052, 3027, 2976, 2929, 1730, 1686, 1595, 1581, 1487, 1446, 1367, 1247, 1148, 1073, 1002, 908, 846, 755, 692 cm^{-1}; *dr* = 95/5, *er* = 92.5/7.5, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 1.0 ml/min, 254 nm UV detector), t_R = 6.5 min (major) and t_R = 12.0 min (minor).

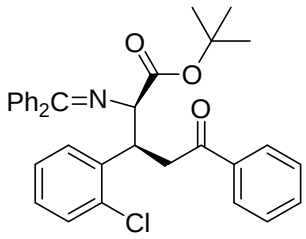


(2*R*,3*S*)-*tert*-Butyl 3-(4-chlorophenyl)-2-(diphenylmethyleneamino)-5-oxo-5-phenylpentanoate (5g): 50.6 mg, 94% yield; $[\alpha]^{20}_{D}$ +58.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (s, 9H), 3.61–3.65 (m, 1H), 3.75–3.80 (m, 1H), 4.16–4.20 (m, 2H), 6.77 (d, *J* = 7.0 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.34–7.39 (m, 5H), 7.41–7.48 (m, 3H), 7.54–7.57 (m, 1H), 7.69–7.70 (m, 2H), 7.97–7.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.6, 171.7, 170.0, 140.2, 139.4, 137.2, 136.4, 133.2, 132.5, 130.7, 130.1, 129.0, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.7, 81.8, 70.9, 44.3, 40.0, 28.1; MS (ESI) m/z 538.18 $[M]^+$; IR (KBr) ν 3050, 3001, 2974, 2928, 1733, 1674, 1621, 1596, 1494, 1446, 1282, 1144, 1089, 1010, 836, 692 cm^{-1}; *dr* = 95/5, *er* = 92/8, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 6.6 min (major) and t_R = 12.3 min (minor).

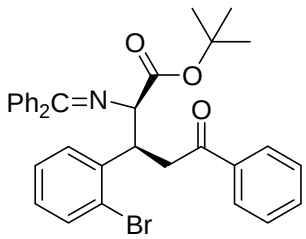


(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-3-(naphthalen-2-yl)-5-oxo-5-phenylpentanoate (5h): 54.3 mg, 98% yield; $[\alpha]^{20}_{D}$ +62.1 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (s, 9H), 3.76–3.80 (m, 1H), 3.94–4.00 (m, 1H), 4.35–4.46 (m, 2H), 6.68 (s, 2H), 7.24–7.26 (m, 2H), 7.33–7.41 (m, 6H), 7.43–7.48 (m, 3H), 7.54–7.57 (m, 1H), 7.66–7.71 (m, 3H), 7.75–7.76 (m, 3H), 8.03–8.04 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.8, 171.6, 170.3, 139.6, 139.2, 137.4, 136.5, 133.6, 133.1, 132.6, 130.6, 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.7, 127.5, 127.1, 126.0, 125.6, 81.6, 71.1, 45.1, 40.3, 28.1; MS (ESI) m/z 554.21 $[M + 1]^+$; IR (KBr) ν 3059, 3028, 2971, 2928, 1734, 1673, 1619, 1596, 1511, 1447, 1365,

1291, 1147, 1013, 826, 701 cm^{-1}; *dr* = 93/7, *er* = 93/7, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 8.3 min (major) and t_R = 17.1 min (minor).

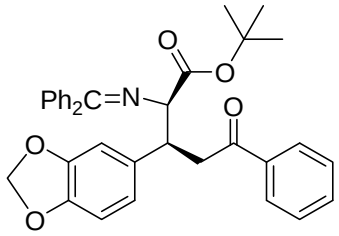


(2*R*,3*S*)-*tert*-Butyl 3-(2-chlorophenyl)-2-(diphenylmethyleneamino)-5-oxo-5-phenylpentanoate (5i): 49.6 mg, 92% yield; $[\alpha]^{20}_D$ +88.9 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.41 (s, 9H), 3.70–3.74 (m, 1H), 4.00–4.06 (m, 1H), 4.33 (d, *J* = 4.0 Hz, 1H), 4.74–4.76 (m, 1H), 6.58 (d, *J* = 5.5 Hz, 2H), 7.14–7.10 (m, 2H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.27–7.31 (m, 3H), 7.34–7.43 (m, 4H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 171.8, 170.2, 139.5, 138.8, 137.2, 136.3, 134.7, 133.1, 130.6, 129.8, 129.3, 129.0, 128.7, 128.6, 128.4, 128.4, 128.2, 127.8, 127.5, 126.5, 81.7, 68.1, 40.9, 38.9, 28.2; MS (ESI) m/z 538.17 $[M]^+$; IR (KBr) ν 3059, 3025, 2977, 2930, 1728, 1687, 1625, 1596, 1475, 1446, 1368, 1291, 1149, 1073, 1036, 1002, 846, 752, 693 cm^{-1}; *dr* = 99/1, *er* = 95.5/4.5,determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 7.1 min (major) and t_R = 9.5 min (minor).

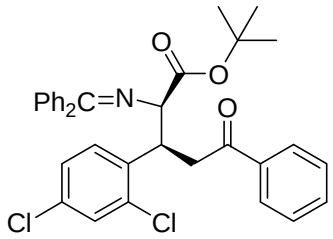


(2*R*,3*S*)-*tert*-Butyl 3-(2-bromophenyl)-2-(diphenylmethyleneamino)-5-oxo-5-phenylpentanoate (5j): 56.0 mg, 96% yield; $[\alpha]^{20}_D$ +93.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 9H), 3.69–3.73 (m, 1H), 4.04–4.09 (m, 1H), 4.31 (d, *J* = 2.5 Hz, 1H), 4.70–4.73 (m, 1H), 6.52 (d, *J* = 4.0 Hz, 2H), 6.98–7.02 (m, 1H),

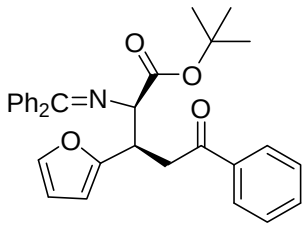
7.08–7.11 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.26–7.29 (m, 2H), 7.33–7.42 (m, 4H), 7.47 (t, *J* = 8.0 Hz, 3H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 8.04 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 171.9, 170.1, 140.3, 139.4, 137.2, 136.3, 133.2, 133.1, 130.6, 129.4, 129.0, 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 127.4, 127.1, 125.7, 81.7, 68.0, 43.3, 38.9, 28.2; MS (ESI) m/z 582.04 $[M + 1]^+$, 584.06 $[M + 1]^+$; IR (KBr) ν 3060, 3021, 2976, 2928, 1728, 1687, 1624, 1597, 1470, 1446, 1368, 1291, 1151, 1022, 1003, 846, 752, 696 cm^{-1}; *dr* = 98/2, *er* = 95/5, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 7.3 min (major) and t_R = 8.8 min (minor).



(2*R*,3*S*)-*tert*-Butyl 3-(benzo[*d*][1,3]dioxol-5-yl)-2-(diphenylmethyleneamino)-5-oxo-5-phenylpentanoate (5k): 51.5 mg, 94% yield; $[\alpha]^{20}_D$ +74.3 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.36 (s, 9H), 3.55–3.59 (m, 1H), 3.64–3.69 (m, 1H), 4.13–4.18 (m, 2H), 5.85 (s, 2H), 6.64–6.67 (m, 3H), 6.87 (d, *J* = 6.5 Hz, 2H), 7.35–7.41 (m, 5H), 7.42–7.47 (m, 3H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.70–7.72 (m, 2H), 7.98–8.00 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.9, 171.4, 170.2, 147.5, 146.3, 139.6, 137.3, 136.5, 135.4, 133.1, 130.6, 129.1, 128.8, 128.7, 128.5, 128.4, 128.3, 127.8, 121.9, 109.2, 108.2, 100.9, 81.5, 71.3, 44.8, 40.6, 28.1; MS (ESI) m/z 548.16 $[M + 1]^+$; IR (KBr) ν 3067, 3023, 2977, 2927, 1728, 1687, 1621, 1597, 1488, 1446, 1368, 1248, 1149, 1039, 935, 695 cm^{-1}; *dr* = 95/5, *er* = 96/4, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 9.8 min (major) and t_R = 20.5 min (minor).

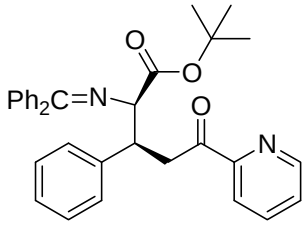


(2*R*,3*S*)-*tert*-Butyl 3-(2,4-dichlorophenyl)-2-(diphenylmethyleneamino)-5-oxo-5-phenylpentanoate (5l): 56.1 mg, 98% yield; $[\alpha]^{20}_{D}$ +68.9 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 9H), 3.70–3.74 (m, 1H), 3.99–4.04 (m, 1H), 4.29 (d, *J* = 2.5 Hz, 1H), 4.66–4.69 (m, 1H), 6.64 (d, *J* = 4.5 Hz, 2H), 7.04–7.14 (m, 2H), 7.30–7.39 (m, 6H), 7.40–7.44 (m, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.67 (d, *J* = 7.5 Hz, 2H), 8.03 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.3, 172.1, 170.0, 139.3, 137.6, 137.0, 136.1, 135.3, 133.3, 132.8, 130.7, 130.1, 129.5, 129.0, 128.8, 128.7, 128.5, 128.4, 128.3, 127.4, 126.7, 81.9, 67.8, 40.4, 38.7, 28.2; MS (ESI) m/z 572.07 $[M]^+$; IR (KBr) ν 3073, 3006, 2974, 2924, 1732, 1673, 1621, 1595, 1476, 1445, 1366, 1285, 1144, 1009, 831, 691 cm^{-1}; *dr* = 98/2, *er* = 95/5, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 6.0 min (major) and t_R = 7.5 min (minor).

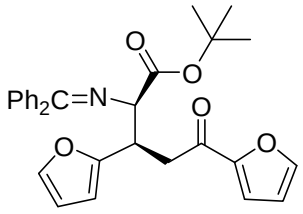


(2*R*,3*R*)-*tert*-Butyl 2-(diphenylmethyleneamino)-3-(furan-2-yl)-5-oxo-5-phenylpentanoate (5m): 48.4 mg, 98% yield; $[\alpha]^{20}_{D}$ +53.4 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42 (s, 9H), 3.58–3.62 (m, 1H), 3.80–3.85 (m, 1H), 4.35–4.38 (m, 2H), 6.02 (d, *J* = 3.0 Hz, 1H), 6.20–6.21 (m, 1H), 6.94 (d, *J* = 6.0 Hz, 2H), 7.21–7.22 (m, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.39–7.43 (m, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 171.7, 170.0, 155.1, 141.2, 139.8, 137.2, 136.5, 133.2, 130.6, 129.1, 128.8, 128.8, 128.5, 128.4, 128.2, 127.9, 110.4, 106.7, 81.7, 68.9, 38.6, 38.5, 28.2; MS (ESI) m/z 494.18 $[M + 1]^+$; IR (KBr) ν 3060, 3019, 2977, 2931, 1730, 1689,

1625, 1597, 1504, 1447, 1368, 1258, 1158, 1013, 847, 701 cm^{-1}; *dr* = 97/3, *er* = 95/5, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 7.2 min (major) and t_R = 25.8 min (minor).

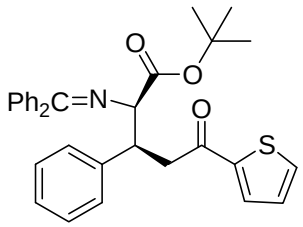


(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-oxo-3-phenyl-5-(pyridin-2-yl) pentanoate (5n): 46.4 mg, 92% yield; $[\alpha]^{20}_D$ +40.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29 (s, 9H), 3.76–3.80 (m, 1H), 3.94–3.99 (m, 1H), 4.21 (d, *J* = 6.0 Hz, 1H), 4.29–4.33 (m, 1H), 6.85 (d, *J* = 6.0 Hz, 2H), 7.10–7.13 (m, 1H), 7.17 (t, *J* = 7.0 Hz, 2H), 7.22 (d, *J* = 7.0 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.34–7.39 (m, 5H), 7.64–7.70 (m, 3H) 7.87 (d, *J* = 8.0 Hz, 1H), 8.67 (d, *J* = 4.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.5, 171.0, 170.2, 153.7, 148.9, 142.0, 139.6, 136.8, 136.6, 130.4, 129.1, 129.0, 128.5, 128.4, 128.2, 128.1, 127.9, 127.0, 126.6, 122.0, 81.2, 71.4, 45.1, 39.7, 28.0; MS (ESI) m/z 505.15 $[M + 1]^+$; IR (KBr) ν 3062, 3027, 2975, 2919, 1728, 1698, 1619, 1582, 1490, 1445, 1367, 1284, 1147, 994, 850, 697 cm^{-1}; *dr* = 94/6, *er* = 94/6, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 90/10, 0.8 ml/min, 254 nm UV detector), t_R = 7.3 min (major) and t_R = 22.1 min (minor).

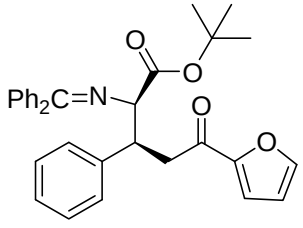


(2*R*,3*R*)-*tert*-Butyl 2-(diphenylmethyleneamino)-3,5-di(furan-2-yl)-5-oxopentanoate (5o): 44.0 mg, 91% yield; $[\alpha]^{20}_D$ +64.1 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.40 (s, 9H), 3.37–3.41 (m, 1H), 3.60–3.65 (m, 1H), 4.30–4.34 (m, 2H), 6.03 (d, *J* = 3.0 Hz, 1H), 6.18–6.19 (m, 1H), 6.50–6.51 (m, 1H), 6.93 (d, *J* = 6.0 Hz, 2H), 7.19–7.20 (m, 1H), 7.25 (d, *J* = 3.5 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H),

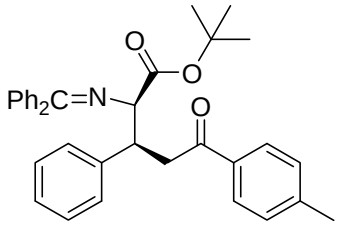
7.38–7.40 (m, 4H), 7.56 (s, 1H), 7.44–7.46 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.5, 171.7, 169.9, 154.8, 152.9, 146.5, 141.3, 139.7, 136.5, 130.6, 129.1, 129.1, 128.8, 128.5, 128.2, 128.1, 127.9, 127.9, 117.5, 112.4, 110.4, 106.9, 81.7, 68.8, 38.6, 38.5, 28.1; MS (ESI) m/z 484.09 $[M + 1]^+$; IR (KBr) ν 3119, 3052, 2977, 2931, 1728, 1679, 1624, 1569, 1504, 1468, 1368, 1290, 1149, 1078, 1011, 908, 845, 734, 696, 597 cm^{-1}; *dr* = 98/2, *er* = 94.5/5.5, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 90/10, 0.8 ml/min, 254 nm UV detector), t_R = 8.7 min (major) and t_R = 25.6 min (minor).



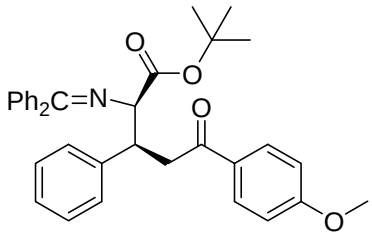
(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-oxo-3-phenyl-5-(thiophen-2-yl) pentanoate (5p): 50.1 mg, 98% yield; $[\alpha]^{20}_D$ +88.0 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (s, 9H), 3.54–3.58 (m, 1H), 3.68–3.73 (m, 1H), 4.20–4.24 (m, 2H), 6.74 (d, *J* = 6.0 Hz, 2H), 7.10–7.19 (m, 6H), 7.32–7.38 (m, 5H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.57 (d, *J* = 4.5 Hz, 1H), 7.71 (d, *J* = 7.0 Hz, 2H), 7.84 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.7, 171.4, 170.2, 144.8, 141.3, 139.6, 136.5, 133.6, 132.1, 130.6, 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 127.7, 126.9, 81.6, 71.1, 45.3, 41.0, 28.1; MS (ESI) m/z 510.12 $[M + 1]^+$; IR (KBr) ν 3062, 3026, 2977, 2931, 1729, 1664, 1623, 1587, 1515, 1413, 1368, 1289, 1147, 1024, 839, 696 cm^{-1}; *dr* = 96/4, *er* = 95/5, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/ 2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 8.8 min (major) and t_R = 23.3 min (minor).



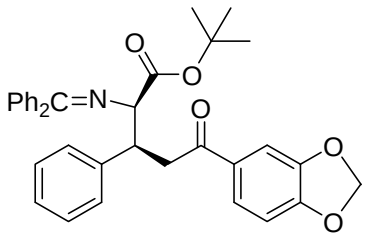
(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-(furan-2-yl)-5-oxo-3-phenyl-pentanoate (5q): 47.0 mg, 95% yield; $[\alpha]^{20}_{D}$ +94.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (s, 9H), 3.42–3.46 (m, 1H), 3.58–3.63 (m, 1H), 4.18–4.24 (m, 2H), 6.46–6.47 (m, 1H), 6.76 (d, *J* = 6.5 Hz, 2H), 7.12–7.18 (m, 6H), 7.32–7.42 (m, 6H), 7.53 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 188.0, 171.4, 170.1, 153.1, 146.3, 141.3, 139.6, 136.5, 130.6, 129.1, 128.8, 128.6, 128.4, 128.3, 128.2, 127.8, 126.8, 117.2, 112.3, 81.5, 71.1, 44.9, 40.3, 28.1; MS (ESI) m/z 494.19 $[M + 1]^+$; IR (KBr) ν 3062, 3023, 2976, 2931, 1730, 1678, 1622, 1568, 1468, 1392, 1368, 1286, 1149, 1028, 846, 766, 698 cm^{-1}; *dr* = 98/2, *er* = 93.5/6.5, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 1.0 ml/min, 254 nm UV detector), t_R = 8.3 min (major) and t_R = 21.6 min (minor).



(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-oxo-3-phenyl-5-p-tolyl-pentanoate (5r): 50.9 mg, 98% yield; $[\alpha]^{20}_{D}$ +66.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 9H), 2.41 (s, 3H), 3.57–3.61 (m, 1H), 3.73–3.78 (m, 1H), 4.18–4.22 (m, 2H), 6.73 (d, *J* = 7.0 Hz, 2H), 7.13–7.17 (m, 5H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.31–7.39 (m, 5H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.5, 171.3, 170.3, 143.7, 141.6, 139.6, 136.5, 134.9, 130.5, 129.4, 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 127.7, 126.7, 81.5, 71.2, 45.1, 40.1, 28.1, 21.9; MS (ESI) m/z 518.16 $[M + 1]^+$; IR (KBr) ν 3058, 3023, 2976, 2929, 1730, 1682, 1607, 1574, 1493, 1446, 1367, 1288, 1148, 1007, 847, 697 cm^{-1}; *dr* = 94/6, *er* = 94/6, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 1.0 ml/min, 254 nm UV detector), t_R = 4.9 min (major) and t_R = 13.1 min (minor).

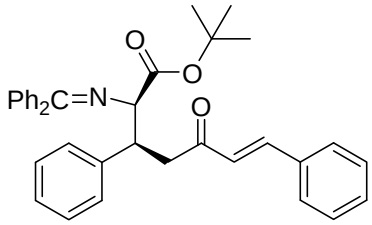


(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-(4-methoxyphenyl)-5-oxo-3-phenylpentanoate (5s): 52.1 mg, 98% yield; $[\alpha]^{20}_{D}$ +56.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 9H), 3.55–3.58 (m, 1H), 3.70–3.76 (m, 1H), 3.86 (s, 3H), 4.19–4.23 (m, 2H), 6.73 (d, *J* = 6.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 7.13–7.17 (m, 5H), 7.31–7.38 (m, 5H), 7.42 (d, *J* = 6.5 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.99 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.4, 171.3, 170.3, 163.5, 141.6, 139.6, 136.5, 130.7, 130.6, 130.5, 129.1, 128.8, 128.6, 128.4, 128.3, 128.2, 127.7, 126.7, 113.8, 81.5, 71.2, 55.6, 45.2, 39.9, 28.1; MS (ESI) m/z 534.22 $[M + 1]^+$; IR (KBr) ν 3067, 3032, 2976, 2929, 1727, 1678, 1599, 1574, 1511, 1446, 1368, 1255, 1149, 1029, 841, 696 cm^{-1}; *dr* = 97/3, *er* = 93.5/6.5, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 12.2 min (major) and t_R = 47.1 min (minor).

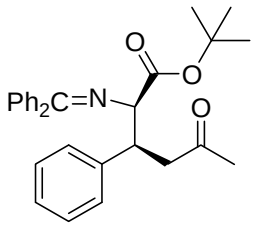


(2*R*,3*S*)-*tert*-Butyl 5-(benzo[*d*][1,3]dioxol-5-yl)-2-(diphenylmethyleneamino)-5-oxo-3-phenylpentanoate (5t): 53.2 mg, 97% yield; $[\alpha]^{20}_{D}$ +65.0 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34 (s, 9H), 3.54–3.57 (m, 1H), 3.66–3.71 (m, 1H), 4.20–4.22 (m, 2H), 5.99(s, 2H), 6.73 (d, *J* = 6.5 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 1H), 7.13–7.18 (m, 5H), 7.31–7.37 (m, 5H), 7.40–7.44 (m, 2H), 7.64–7.66 (m, 1H), 7.71 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9, 171.4, 170.2, 151.7, 148.3, 141.6, 139.6, 136.5, 132.3, 130.6, 129.1, 128.8, 128.6, 128.5, 128.4, 128.3, 127.7, 126.8, 124.6, 108.3, 108.0, 102.0, 81.5, 71.2, 45.3, 40.0, 28.1; MS (ESI) m/z 548.14 $[M + 1]^+$; IR (KBr) ν 3060, 3023, 2976, 2928, 1728, 1678, 1614, 1594, 1487, 1443,

1367, 1254, 1148, 1037, 846, 697 cm^{-1}; *dr* = 98/2, *er* = 96.5/3.5, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 13.2 min (major) and t_R = 33.1 min (minor).

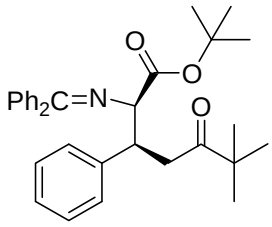


(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-oxo-3,7-diphenylhept-6-enoate (5u): 52.2 mg, 98% yield; $[\alpha]^{20}_D$ +44.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 9H), 3.31–3.36 (m, 1H), 3.43–3.49 (m, 1H), 4.26–4.22 (m, 2H), 6.77–6.81 (m, 2H), 7.17–7.24 (m, 5H), 7.33–7.45 (m, 10H), 7.54–7.61 (m, 3H), 7.74 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 171.2, 170.0, 142.5, 141.1, 139.4, 136.3, 134.7, 130.4, 130.3, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.2, 128.1, 127.6, 126.7, 126.2, 81.3, 71.0, 45.0, 42.7, 27.9; MS (ESI) m/z 530.64 $[M + 1]^+$; IR (KBr) ν 3059, 3029, 2976, 2929, 1728, 1685, 1611, 1489, 1449, 1362, 1327, 1285, 1153, 1079, 977, 786, 697 cm^{-1}; *dr* = 97/3, *er* = 91/9, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 90/10, 1.0 ml/min, 254 nm UV detector), t_R = 11.8 min (major) and t_R = 21.8 min (minor).



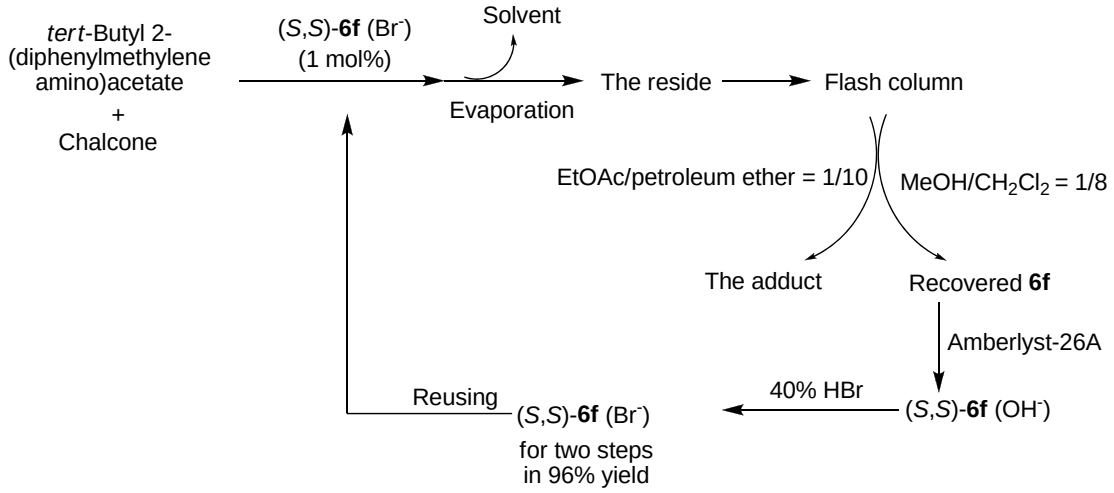
(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-5-oxo-3-phenylhexanoate (5v): 37.1 mg, 84% yield; $[\alpha]^{20}_D$ +96.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (s, 9H), 2.09 (s, 3H), 3.05–3.09 (m, 1H), 3.13–3.18 (m, 1H), 4.00–4.04 (m, 1H), 4.09 (d, *J* = 5.5 Hz, 1H), 6.73 (d, *J* = 7.0 Hz, 2H), 7.13–7.21 (m, 5H), 7.30–7.38 (m, 5H), 7.39–7.42 (m, 1H), 7.67–7.69 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.6, 171.3, 170.2, 141.4, 139.5, 136.4, 130.6, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 127.7,

126.9, 81.5, 71.1, 45.5, 44.8, 30.6, 28.1; MS (ESI) m/z 442.10 $[M + 1]^+$; IR (KBr) ν 3060, 3028, 2977, 2931, 1724, 1659, 1623, 1597, 1575, 1492, 1446, 1392, 1367, 1250, 1149, 1083, 1028, 846, 765, 699 cm^{-1}; *dr* = 93/7, *er* = 90.5/9.5, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 95/5, 1.0 ml/min, 254 nm UV detector), t_R = 6.7 min (major) and t_R = 8.3 min (minor).



(2*R*,3*S*)-*tert*-Butyl 2-(diphenylmethyleneamino)-6,6-dimethyl-5-oxo-3-phenyl-heptanoate (5w): 28.0 mg, 57% yield; $[\alpha]^{20}_D$ +108.7 (*c* 1.0, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) δ 1.05 (s, 9H), 1.33 (s, 9H), 3.00–3.05 (m, 1H), 3.32–3.38 (m, 1H), 4.02–4.05 (m, 1H), 4.11 (d, *J* = 5.5 Hz, 1H), 6.71 (d, *J* = 6.5 Hz, 2H), 7.11–7.19 (m, 5H), 7.29–7.37 (m, 5H), 7.40–7.42 (m, 1H), 7.67–7.69 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.9, 171.1, 170.3, 142.0, 139.6, 136.6, 130.5, 129.0, 128.8, 128.5, 128.4, 128.3, 128.2, 127.7, 126.6, 81.3, 70.9, 44.3, 44.3, 38.2, 28.1, 26.5; MS (ESI) m/z 484.17 $[M + 1]^+$; IR (KBr) ν 3057, 3032, 2970, 2924, 1727, 1708, 1613, 1480, 1444, 1367, 1285, 1148, 1070, 850, 779, 699 cm^{-1}, *dr* = 99/1, *er* = 91/9, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 95/5, 0.5 ml/min, 254 nm UV detector), t_R = 12.4 min (major) and t_R = 14.8 min (minor).

5. Large-scale Synthesis and Recovery of Catalyst 6f:



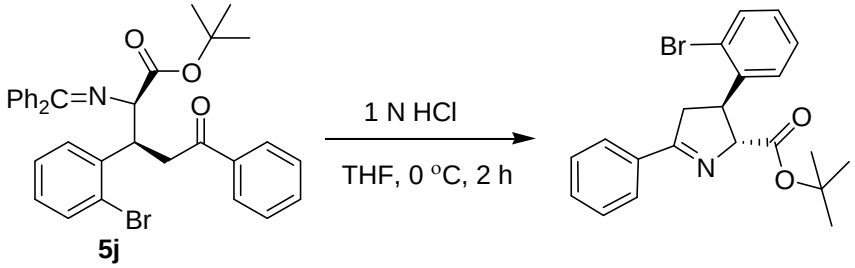
N-(diphenylmethylene)glycine *tert*-butyl ester **3** (11.8 g, 40 mmol) was added to a mixture of 3-(2-bromophenyl)-1-phenylprop-2-en-1-one **4j** (12.1 g, 42 mmol), (*S*,*S*)-**6f** (1.17 g, 0.4 mmol) and Cs_2CO_3 (6.5 g, 20 mmol) in xylene (200 mL) under argon atmosphere, the resulting solution was stirred at 30 °C for 12 h. The resulting mixture was purified by column chromatographyon silica gel (AcOEt/petroleum ether = 1/10 as eluant) to furnish the conjugate adducts **5j** (21.4 g, 92% yield, *dr* = 98/2, *er* = 95/5, determined by HPLC analysis). The catalyst **6f** was recovered (MeOH/ CH_2Cl_2 = 1/8 as eluant) in almost quantitative yield.

Anion exchange of recovered catalyst **6f** using Amberlyst-26A (OH^- form) gave (*S*,*S*)-**6f** (OH^-). The methanol solution of (*S*,*S*)-**6f** (OH^-) was treated with 40% HBr aqueous solution (excess) at room temperature. The resulting mixture was poured into water and extracted with CH_2Cl_2. The organic extracts were washed with 5% K_2CO_3 aqueous solution and dried over $MgSO_4$. Evaporation of solvents gave reactivated catalyst (*S*,*S*)-**6f** (Br^-) of 1.12 g in 96% yield.

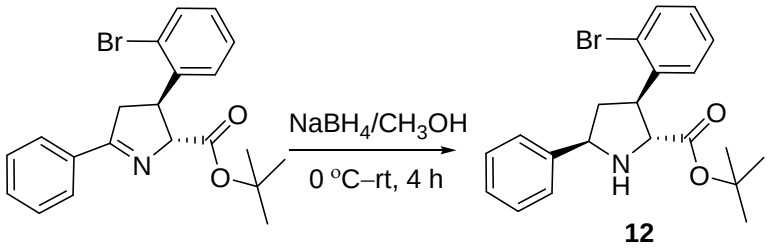
N-(diphenylmethylene)glycine *tert*-butyl ester **3** (29.5 mg, 0.1 mmol) was added to a mixture of 3-(2-bromophenyl)-1-phenylprop-2-en-1-one **4j** (30.1 mg, 0.105 mmol), recovered (*S*,*S*)-**6f** (2.9 mg, 0.001 mmol) and Cs_2CO_3 (16.3 mg, 0.05 mmol) in xylene (0.5 mL) under argon atmosphere, the resulting solution was stirred at 30 °C for 12 h. The resulting mixture was purified by column chromatographyon silica gel (AcOEt/

petroleum ether = 1/10 as eluant) to furnish the conjugate adducts **5j** (54.9 mg, 94% yield, *dr* = 98/2, *er* = 95/5 determined by HPLC analysis).

6. Synthetic Transformations of the Adducts 5:

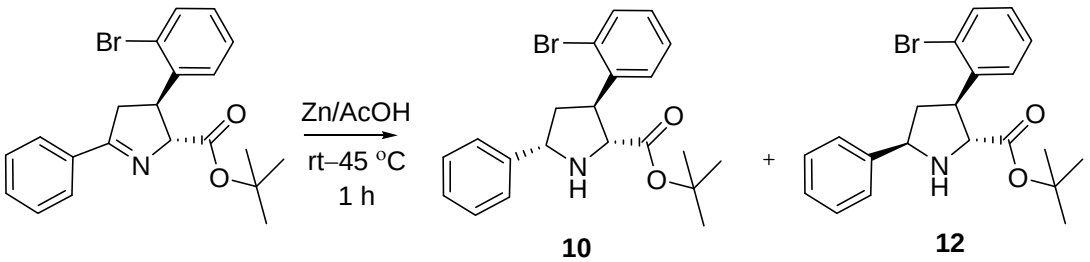


(2*R*,3*S*)-*tert*-Butyl 3-(2-bromophenyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate:[1] 1 N hydrochloric acid (3.0 mL) was added to a solution of **5j** (174.8mg, 0.3 mmol) in THF (3.0 mL) at 0 °C, and stirring was maintained for 2 h. The resulting mixture was neutralized by addition of solid $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatographyon silica gel (AcOEt/petroleum ether = 1/10 as eluant) to afford (2*R*,3*S*)-*tert*-Butyl 3-(2-bromophenyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate (120.1 mg, 0.3 mmol) in quantitative yield. $[\alpha]^{20}_{D}$ –59.0 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48 (s, 9H), 3.07–3.11 (m, 1H), 3.66-3.72 (m, 1H), 4.25–4.29 (m, 1H), 4.93–4.95 (m, 1H), 7.08–7.11 (m, 1H), 7.14–7.16 (m, 1H), 7.24–7.28 (m, 1H), 7.42–7.49 (m, 3H), 7.58–7.60 (m, 1H), 7.91–7.93 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 171.2, 143.1, 133.8, 133.3, 131.3, 128.7, 128.5, 128.4, 128.3, 127.9, 124.3, 82.5, 81.8, 45.8, 44.4, 28.2; MS (ESI) m/z 400.07 $[M + 1]^+$, 402.06 $[M + 1]^+$; IR (KBr) ν 3047, 3011, 2980, 2929, 1726, 1615, 1576, 1472, 1446, 1367, 1244, 1147, 1024, 795, 760, 695 cm^{-1}; *er* = 95/5, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 95/5, 1.0 ml/min, 254 nm UV detector), t_R = 15.4 min (major) and t_R = 16.7 min (minor).



12

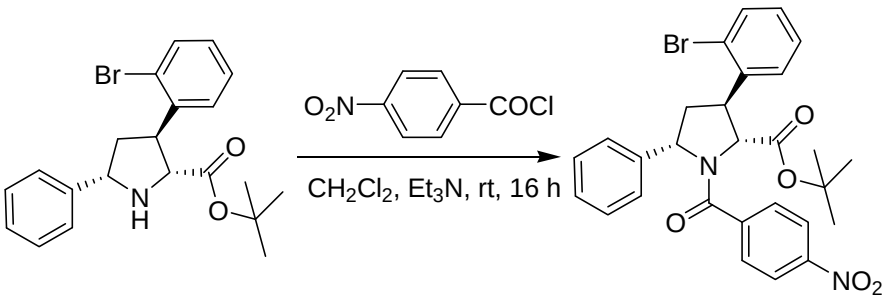
(2*R*,3*S*,5*R*)-*tert*-Butyl 3-(2-bromophenyl)-5-phenylpyrrolidine-2-carboxylate (12): To a solution of (2*R*,3*S*)-*tert*-butyl 3-(2-bromophenyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate (80.1 mg, 0.2 mmol) in 2 mL of MeOH was added $NaBH_4$ (37.8 mg, 1.0 mmol) in portions at 0 °C. The resultant mixture was stirred for 4 h at room temperature (monitored by TLC). The mixture was evaporated *in vacuo*, added water (5 mL), and extracted with dichloromethane (5 mL × 3), washed with brine and dried with $MgSO_4$. Concentration and flash chromatography (AcOEt/petroleum ether = 1/20 as eluant) afforded (2*R*,3*S*,5*R*)-*tert*-butyl 3-(2-bromophenyl)-5-phenyl-pyrrolidine-2-carboxylate **12** (50.6 mg, 0.126 mmol, 63% yield) as a colorless oil. $[\alpha]^{20}_D$ −7.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (s, 9H), 1.78–1.82 (m, 1H), 2.65–2.72 (m, 2H), 3.99–4.07 (m, 2H), 4.56–4.60 (m, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.25–7.38 (m, 4H), 7.49–7.58 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8, 143.9, 142.5, 132.6, 128.4, 128.3, 128.0, 127.9, 127.1, 126.5, 124.5, 81.4, 67.4, 62.4, 48.9, 45.1, 27.9; MS (ESI) m/z 402.15 $[M + 1]^+$, 404.10 $[M + 1]^+$; IR (KBr) ν 3343, 3061, 3027, 2976, 2931, 1727, 1603, 1474, 1440, 1368, 1230, 1155, 1024, 846, 752, 700 cm^{-1}; *er* = 95/5, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/ 2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 9.4 min (major) and t_R = 11.7 min (minor).



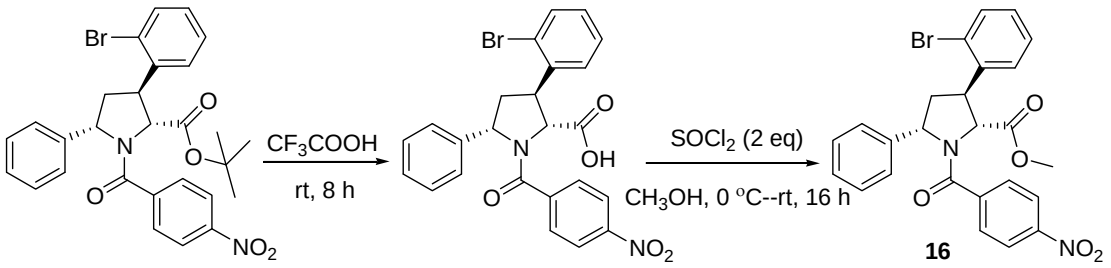
10 **12**

***tert*-Butyl 3-(2-bromophenyl)-5-phenylpyrrolidine-2-carboxylate**: To a solution of (2*R*,3*S*)-*tert*-butyl 3-(2-bromophenyl)-5-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate (80.1 mg, 0.2 mmol) in 2 mL of AcOH was added Zinc powder (30 equiv) in portions at room temperature. The resultant mixture was stirred for 1 h at 45 ^{o}C (monitored by TLC). After Zinc powder was filtered off, the filtrate was cooled to 0 ^{o}C. The filtrate was diluted with ethyl acetate and neutralized by the addition of sodium hydrogen carbonate (70% saturated *aq*). The mixture was extracted with dichloromethane (10 mL × 4), washed with brine and dried with $MgSO_4$. Concentration and flash chromatography (AcOEt/petroleum ether = 1/20–1/4 as eluant) afforded both (2*R*,3*S*,5*S*)-*tert*-butyl 3-(2-bromophenyl)-5-phenylpyrrolidine-2-carboxylate **10** (39.2 mg, 0.097 mmol, 48% yield) as a colorless oil and (2*R*,3*S*,5*R*)-*tert*-butyl 3-(2-bromophenyl)-5-phenylpyrrolidine-2-carboxylate **12** (12.2 mg, 0.030 mmol, 15% yield).

(2*R*,3*S*,5*S*)-*tert*-butyl 3-(2-bromophenyl)-5-phenylpyrrolidine-2-carboxylate (**10**): $[\alpha]^{20}_{D}$ –26.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.41 (s, 9H), 2.19–2.24 (m, 1H), 2.28–2.34 (m, 1H), 2.62 (s, 1H), 3.96 (d, *J* = 6.5 Hz, 1H), 4.01–4.05 (m, 1H), 4.46 (t, *J* = 6.5 Hz, 1H), 7.10–7.13 (m, 1H), 7.26–7.29 (m, 1H), 7.34–7.38 (m, 3H), 7.47–7.50 (m, 3H), 7.57–7.59 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.2, 143.7, 142.2, 133.1, 128.8, 128.3, 128.2, 128.2, 128.0, 127.5, 126.9, 124.9, 81.7, 67.7, 62.4, 49.3, 42.9, 28.1; MS (ESI) m/z 402.03 $[M + 1]^+$, 404.05 $[M + 1]^+$; IR (KBr) ν 3359, 3060, 2976, 2930, 1727, 1472, 1392, 1367, 1246, 1155, 1023, 846, 753, 700 cm^{-1}; *er* = 95/5, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 95/5, 0.8 ml/min, 254 nm UV detector), t_R = 9.4 min (minor) and t_R = 17.2 min (major).

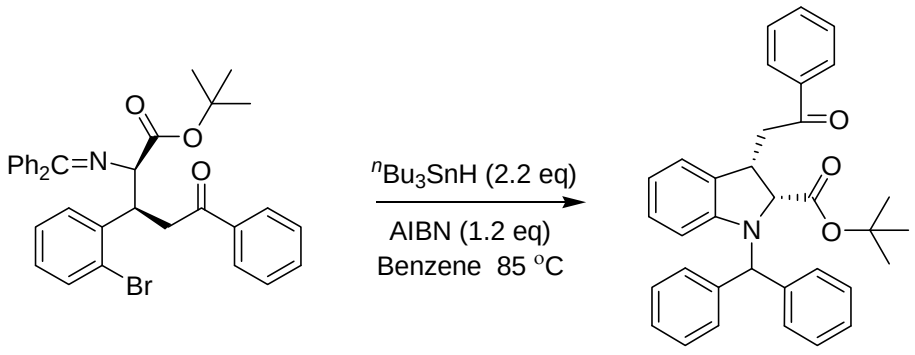


(2*R*,3*S*,5*S*)-*tert*-Butyl 3-(2-bromophenyl)-1-(4-nitrobenzoyl)-5-phenylpyrrolidine-2-carboxylate: (2*R*,3*S*,5*S*)-*tert*-Butyl 3-(2-bromophenyl)-5-phenylpyrrolidine-2-carboxylate **10** (40.2 mg, 0.1 mmol) was dropped to a mixture of 4-nitrobenzoyl chloride (37.1 mg, 0.2 mmol) and Et_3N (41.8 μl, 0.3 mmol) in dry CH_2Cl_2 (1.5 mL) at 0 °C under argon atmosphere, then stirring was maintained for 16 h at room temperature. The resulting mixture was quenched with aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatographyon silica gel (AcOEt/petroleum ether = 1/4 as eluant) to afford the product (48.0 mg, 0.087 mmol, 87% yield) as a white solid. Mp 70–72 °C; $[\alpha]^{20}_D$ –34.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47 (s, 9H), 2.37–2.48 (m, 2H), 4.19–4.23 (m, 1H), 4.81–4.83 (m, 1H), 4.87 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 2H), 8.24–8.30 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5, 169.2, 148.3, 142.1, 142.7, 138.3, 133.3, 128.9, 128.8, 127.9, 127.7, 127.3, 126.7, 124.9, 123.5, 123.1, 82.2, 66.5, 58.4, 44.4, 43.1, 28.0; MS (ESI) m/z 573.05 $[M + Na]^+$, 575.05 $[M + Na]^+$; IR (KBr) ν 3062, 2975, 2929, 2868, 1739, 1646, 1601, 1524, 1417, 1346, 1224, 1148, 1024, 850, 758, 702 cm^{-1}; *er* = 95/5, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 70/30, 1.0 ml/min, 254 nm UV detector), t_R = 24.8 min (minor) and t_R = 35.6 min (major).



(2*R*,3*S*,5*S*)-Methyl 3-(2-bromophenyl)-1-(4-nitrobenzoyl)-5-phenylpyrrolidine-2-carboxylate (16): *tert*-Butyl 3-(2-bromophenyl)-1-(4-nitrobenzoyl)-5-phenyl-pyrrolidine-2-carboxylate (48.0 mg, 0.087 mmol) was stirred in neat trifluoroacetic acid (4 mL) for 8 h at room temperature. The mixture was evaporated *in vacuo*, and

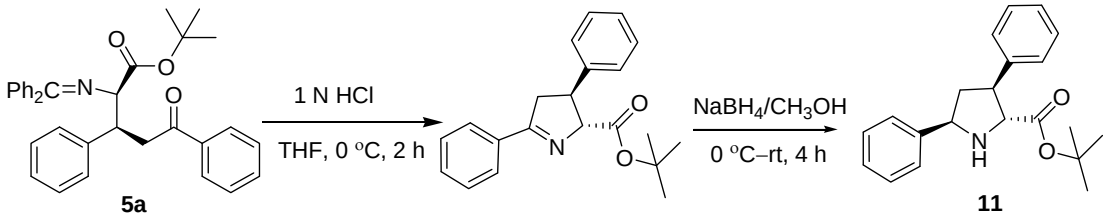
purified by flash column chromatographyon silica gel (AcOEt/petroleum ether = 1/1 as eluant) to afford 3-(2-bromophenyl)-1-(4-nitrobenzoyl)-5-phenylpyrrolidine-2-carboxylic acid**.** $SOCl_2$ (12.7 μL, 0.128 mmol) was dropped to a solution of 3-(2-bromophenyl)-1-(4-nitrobenzoyl)-5-phenylpyrrolidine-2-carboxylic acid (43.0 mg, 0.087 mmol) in dry methanol (2 mL) at 0 °C, then stirring was maintained for 16 h at room temperature. The mixture was evaporated *in vacuo*, and purified by column chromatographyon silica gel (AcOEt/petroleum ether = 1/4 as eluant) to afford the product **16** (40.7 mg, 0.080 mmol, 92% yield)**.** Recrystallization of this product from AcOEt/hexane furnished suitable crystals for X-ray structure analysis. Mp 86–89 °C; $[\alpha]^{20}_{D}$ −63.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48–2.56 (m, 2H), 3.86 (s, 3H), 4.19–4.23 (m, 1H), 4.85–4.87 (m, 1H), 4.97 (d, *J* = 5.2 Hz, 1H), 7.20–7.27 (m, 4H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.41–7.49 (m, 4H), 7.63 (d, *J* = 6.4 Hz, 1H), 7.98 (d, *J* = 6.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 169.1, 148.3, 141.7, 138.3, 133.6, 129.1, 128.8, 128.1, 127.8, 127.7, 126.7, 124.9, 123.1, 65.6, 63.6, 52.8, 44.3, 42.9; MS (ESI) m/z 509.02 $[M + 1]^+$, 511.04 $[M + 1]^+$; IR (KBr) ν 2955, 2919, 2847, 1737, 1645, 1593, 1399, 1386, 1359, 1209, 1152, 1019, 827, 758, 707 cm^{-1}; *dr* > 99.9/0.1, *er* = 95/5 (>99.9/0.1 after recrystallization), determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 50/50, 0.8 ml/min, 254 nm UV detector), t_R = 28.3 min (major) and t_R = 60.3 min (minor).



5j **15**

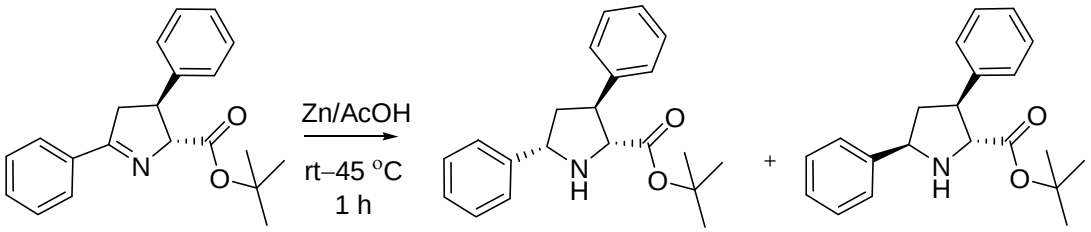
(2*R*,3*S*)-*tert*-Butyl 1-benzhydryl-3-(2-oxo-2-phenylethyl)indoline-2-carboxylate (17):[2] A benzene solution of the **5j** (99.5 mg, 0.17 mmol) and ^{n}Bu$_3$SnH (110.6 mg, 0.38 mmol) was warmed to 85 °C under argon atmosphere. AIBN (34.5 mg, 0.21

mmol) was added as a benzene solution by syringe pump over a 4–5 hour period. The solution was refluxed an additional hour, cooled, and concentrated. The residue was treated with a 1/1 (v/v) ether–satd *aq* KF solution and stirred vigorously until a white precipitate formed. The organic layer was washed with water, dried with $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatographyon silica gel (AcOEt/petroleum ether = 1/10 as eluant) to afford the product **17** (70.7 mg, 0.14 mmol, 82% yield) as a whiter solid**.** Mp 58–60 ^oC; $[\alpha]^{20}_D$ +112.0 (*c* 1.0, CH_2Cl_2); ^1H NMR (500 MHz, $CDCl_3$) δ 1.05 (s, 9H), 3.29–3.34 (m, 1H), 3.52–3.57 (m, 1H), 4.37–4.42 (m, 2H), 5.59 (s, 1H), 6.02 (d, *J* = 7.5 Hz, 1H), 6.66 (t, *J* = 7.5 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.28–7.32 (m, 4H), 7.41 (d, *J* = 7.0 Hz, 2H), 7.46–7.49 (m, 4H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.99–8.01 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.7, 170.6, 151.4, 142.8, 140.5, 136.8, 133.5, 131.2, 129.8, 128.9, 128.8, 128.2, 127.9, 127.7, 127.2, 127.1, 122.1, 118.1, 109.7, 81.5, 69.9, 67.2, 39.6, 38.7, 28.0; MS (ESI) m/z 503.98 $[M]^+$; IR (KBr) ν 3052, 3027, 2958, 2924, 2858, 1728, 1689, 1604, 1480, 1451, 1367, 1217, 1146, 1028, 1001, 845, 746, 704 cm^{-1}; *dr* = 98/2, *er* = 95/5, determined by HPLC analysis (Chiralpak OD-H, *n*-hexane/2-propanol = 90/10, 0.8 ml/min, 254 nm UV detector), t_R = 11.4 min (minor) and t_R = 16.8 min (major).



(2*R*,3*S*,5*R*)-*tert*-Butyl 3,5-diphenylpyrrolidine-2-carboxylate (11): 1 N hydrochloric acid (2.0 mL) was added to a solution of **5a** (100.7mg, 0.2 mmol) in THF (2.0 mL) at 0 ^oC, and stirring was maintained for 2 h. The resulting mixture was neutralized by addition of solid $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over $MgSO_4$ and concentrated. The residue was purified by column chromato- graphyon silica gel (AcOEt/petroleum ether = 1/20 as eluant) to afford (2*R*,3*S*)-*tert*- butyl 3,5-diphenyl-3,4-dihydro-2H-pyrrole-2-carboxylate in

quantitative yield. To a solution of (2*R*,3*S*)-*tert*-butyl 3,5-diphenyl-3,4-dihydro-2H-pyrrole-2-carboxylate (64.3 mg, 0.2 mmol) in 2 mL of MeOH was added $NaBH_4$ (37.8 mg 1.0 mmol) in portions at 0 °C. The resultant mixture was stirred for 4 h at room temperature (monitored by TLC). The mixture was evaporated *in vacuo*, added water (5 mL), and extracted with dichloromethane (5 mL × 3), washed with brine and dried with $MgSO_4$. Concentration and flash chromatography (AcOEt/petroleum ether = 1/20 as eluant) afforded (2*R*,3*S*,5*R*)-*tert*-butyl 3,5-diphenylpyrrolidine-2-carboxylate **11** (37.6 mg, 0.116 mmol, 58% yield) as a colorless oil. $[\alpha]^{20}_{D}$ +18.6 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.44 (s, 9H), 2.01–2.10 (m, 1H), 2.62–2.65 (m, 1H), 2.81 (s, 1H), 3.45 (d, *J* = 7.2 Hz, 1H), 3.95 (d, *J* = 3.6 Hz, 1H), 4.56 (d, *J* = 5.2 Hz, 1H), 7.29 (d, *J* = 4.8 Hz, 2H), 7.39 (s, 6H), 7.52 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.3, 144.1, 142.7, 128.5, 128.4, 127.6, 127.0, 126.6, 126.5, 81.2, 67.9, 62.4, 51.1, 45.1, 28.0; MS (ESI) m/z 324.19 $[M + 1]^+$; IR (KBr) ν 3344, 3061, 3028, 2977, 2932, 1725, 1603, 1492, 1457, 1367, 1228, 1157, 1028, 846, 753, 699 cm^{-1}; *er* = 96/4 determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 95/5, 1.0 ml/min, 254 nm UV detector), t_R = 7.4 min (major) and t_R = 10.7 min (minor).

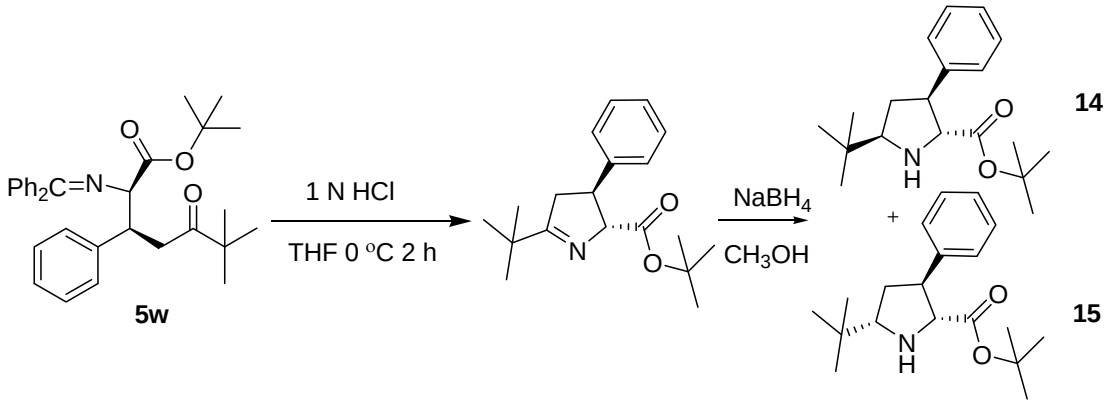


9 **11**

***tert*-Butyl 3,5-diphenylpyrrolidine-2-carboxylate:** To a solution of (2*R*,3*S*)-*tert*-butyl 3,5-diphenyl-3,4-dihydro-2H-pyrrole-2-carboxylate (64.3 mg, 0.2 mmol) in 2 mL of AcOH was added Zinc powder (30 equiv) in portions at room temperature. The resultant mixture was stirred for 1 h at 45 °C (monitored by TLC). After Zinc powder was filtered off, the filtrate was cooled to 0 °C. The filtrate was diluted with ethyl acetate and neutralized by the addition of sodium hydrogen carbonate (70% saturated *aq*). The mixture was extracted with dichloromethane (10

mL × 4), washed with brine and dried with $MgSO_4$. Concentration and flash chromatography (AcOEt/petroleum ether = 1/20–1/4 as eluant) afforded both (2*R*,3*S*,5*S*)-*tert*-butyl 3,5-diphenylpyrrolidine-2-carboxylate **9** (35.0 mg, 0.108 mmol, 54% yield) as a colorless oil and (2*R*,3*S*,5*R*)-*tert*-butyl 3,5-diphenylpyrrolidine-2-carboxylate **11** (11.1 mg, 0.034 mmol, 17% yield).

(2*R*,3*S*,5*S*)-*tert*-Butyl 3,5-diphenylpyrrolidine-2-carboxylate (**9**): $[\alpha]^{20}_{D}$ –34.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.42 (s, 9H), 2.25–2.32 (m, 1H), 2.39–2.46 (m, 1H), 2.50 (s, 1H), 3.46–3.52 (m, 1H), 3.90 (d, *J* = 7.6 Hz, 1H), 4.55 (t, *J* = 7.6 Hz, 1H), 7.28–7.31 (m, 2H), 7.34–7.41 (m, 6H), 7.51 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 143.9, 142.8, 128.6, 128.5, 127.5, 127.2, 126.7, 126.6, 81.3, 68.8, 62.4, 49.9, 43.4, 28.0; MS (ESI) m/z 324.07 $[M + 1]^+$; IR (KBr) ν 3375, 3067, 2970, 2929, 1724, 1603, 1501, 1454, 1367, 1244, 1153, 1029, 845, 756, 700 cm^{-1}; *er* = 96/4, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 95/5, 1.0 ml/min, 254 nm UV detector), t_R = 10.4 min (minor) and t_R = 16.8 min (major).

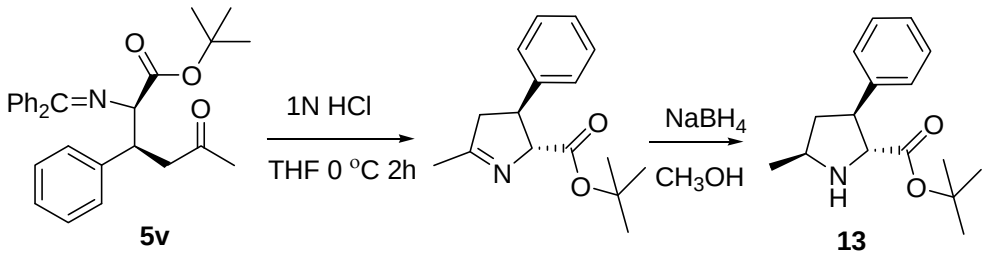


***tert*-Butyl 5-tert-butyl-3-phenylpyrrolidine-2-carboxylate:** 1 N hydrochloric acid (2.0 mL) was added to a solution of **5w** (96.6 mg, 0.2 mmol) in THF (2.0 mL) at 0 °C, and stirring was maintained for 2 h. The resulting mixture was neutralized by addition of solid $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatographyon silica gel (AcOEt/petroleum ether = 1/10 as eluant) to afford (2*R*,3*S*)-*tert*-butyl 5-*tert*-butyl-3-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate in quantitative yield. To a solution of (2*R*,3*S*)-*tert*-butyl 5-*tert*-butyl-3-phenyl-3,4-dihydro-2H-pyrrole-2-

carboxylate (60.2 mg, 0.2 mmol) in 2 mL of MeOH was added $NaBH_4$ (37.8 mg 1.0 mmol) in portions at 0 ^oC. The resultant mixture was stirred for 3 h at room temperature (monitored by TLC). The mixture was evaporated *in vacuo*, added water (5 mL), and extracted with dichloromethane (5 mL × 3), washed with brine and dried with $MgSO_4$. Concentration and flash chromatography (AcOEt/petroleum ether = 1/10 as eluant) afforded both (2*R*,3*S*,5*R*)-*tert*-butyl 5-*tert*-butyl-3-phenylpyrrolidine-2-carboxylate **14** (36.3 mg, 0.120 mmol, 60% yield) as a colorless oil and (2*R*,3*S*,5*S*)-*tert*-butyl 5-*tert*-butyl-3-phenylpyrrolidine-2-carboxylate **15** (8.6 mg, 0.028 mmol, 14% yield) as a colorless oil.

(2*R*,3*S*,5*R*)-*tert*-butyl 5-*tert*-butyl-3-phenylpyrrolidine-2-carboxylate (**14**): $[\alpha]^{20}_D$ –37.1 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (s, 9H), 1.31 (s, 9H), 1.76–1.84 (m, 1H), 2.14–2.20 (m, 1H), 2.50 (s, 1H), 3.13–3.21 (m, 2H), 3.66 (d, *J* = 8.8 Hz, 1H), 7.21–7.25 (m, 1H), 7.28–7.35 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 142.5, 128.3, 127.5, 126.5, 80.9, 68.2, 67.9, 51.9, 37.3, 33.5, 27.9, 26.3; MS (ESI) m/z 304.17 $[M + 1]^+$; IR (KBr) ν 3351, 3029, 2955, 2867, 1726, 1478, 1455, 1367, 1227, 1158, 847, 760, 699 cm^{-1}; *er* = 91/9, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 99/1, 0.8 ml/min, 254 nm UV detector), t_R = 13.7 min (major) and t_R = 28.0 min (minor).

(2*R*,3*S*,5*S*)-*tert*-butyl 5-*tert*-butyl-3-phenylpyrrolidine-2-carboxylate (**15**): $[\alpha]^{20}_D$ –43.0 (*c* 1.0, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$) δ 1.00 (s, 9H), 1.35 (s, 9H), 1.87–1.94 (m, 1H), 2.04–2.11 (m, 1H), 2.19 (s, 1H), 3.13–3.21 (m, 2H), 3.66 (d, *J* = 8.0 Hz, 1H), 7.22–7.28 (m, 3H), 7.30–7.34 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 143.4, 128.4, 127.5, 126.4, 81.0, 69.1, 68.5, 51.1, 36.8, 33.1, 27.9, 26.5; MS (ESI) m/z 304.07 $[M + 1]^+$; IR (KBr) ν 3306, 3026, 2960, 2869, 1727, 1476, 1458, 1367, 1255, 1158, 848, 761, 699 cm^{-1}; *er* = 91/9, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 99/1, 0.8 ml/min, 254 nm UV detector), t_R = 8.5 min (minor) and t_R = 9.9 min (major).



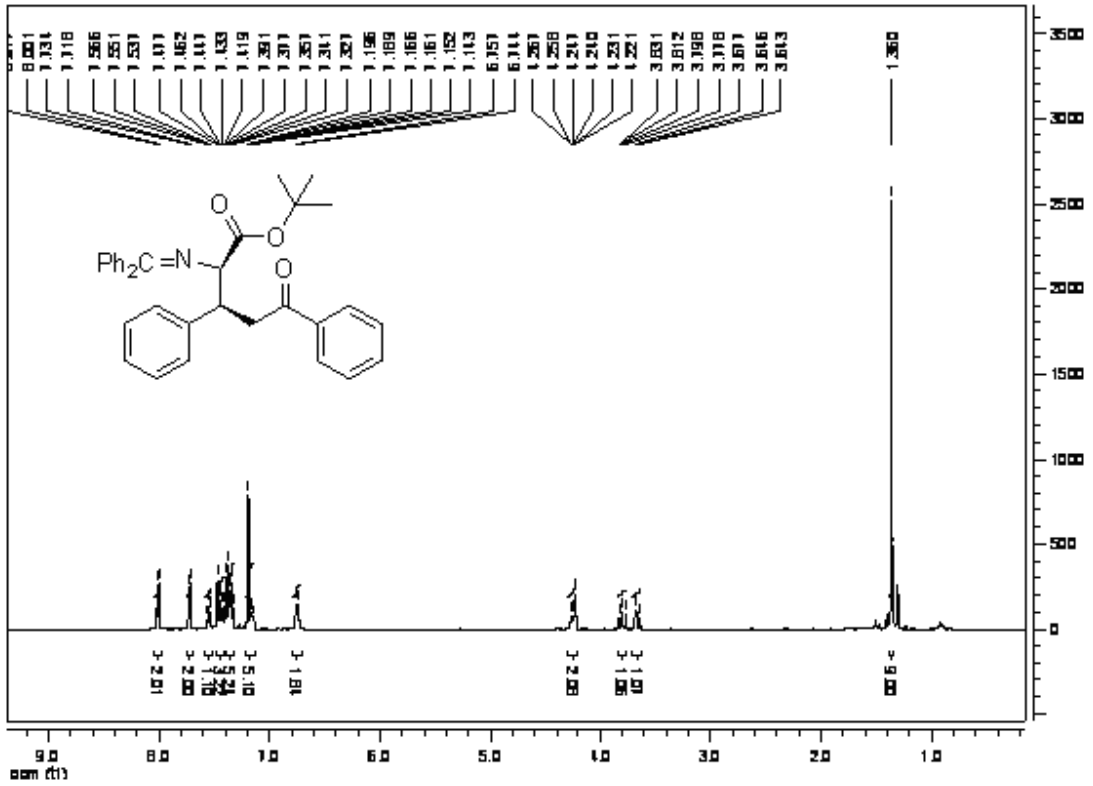
5v **13**

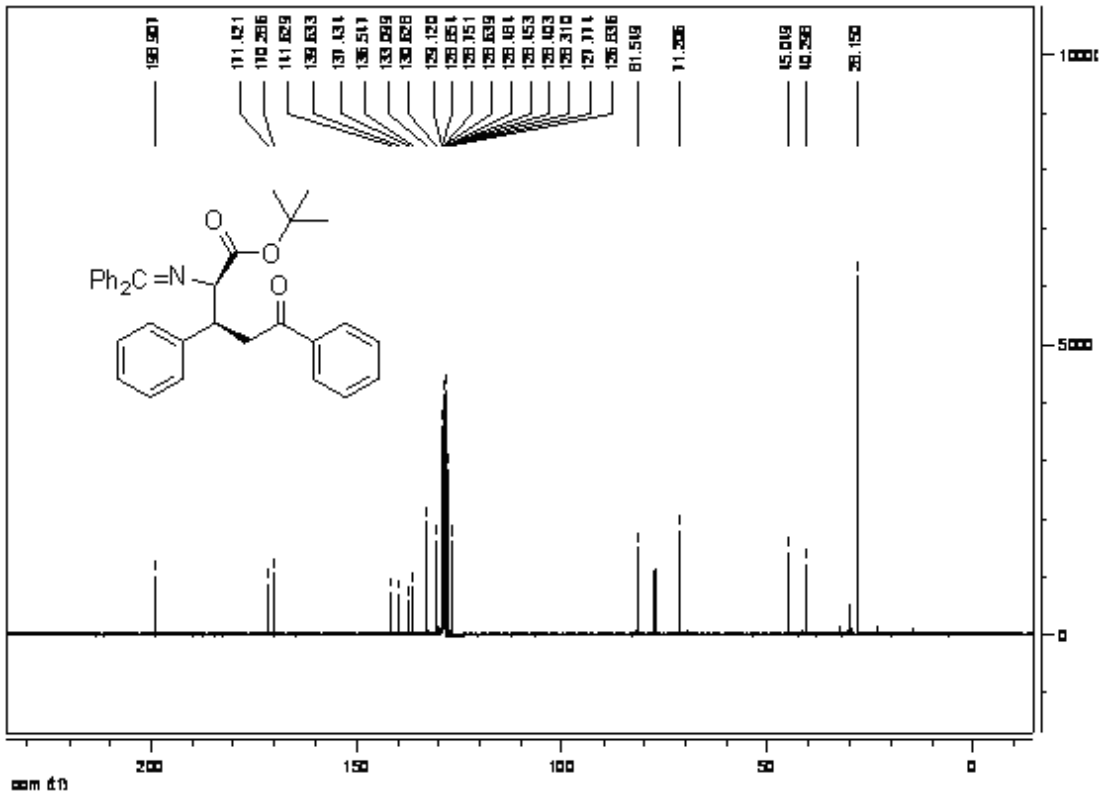
(2*R*,3*S*,5*S*)-*tert*-Butyl 5-methyl-3-phenylpyrrolidine-2-carboxylate (13): 1N hydrochloric acid (2.0 mL) was added to a solution of **5v** (88.4 mg, 0.2 mmol) in THF (2.0 mL) at 0 °C, and stirring was maintained for 2 h. The resulting mixture was neutralized by addition of solid $NaHCO_3$ and extracted with CH_2Cl_2. The organic extracts were dried over $MgSO_4$ and concentrated. The residue was purified by column chromatographyon silica gel (AcOEt/petroleum ether = 1/1 as eluant) to afford (2*R*,3*S*)-*tert*-butyl 5-methyl-3-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate in quantitative yield. To a solution of (2*R*,3*S*)-*tert*-butyl 5-methyl-3-phenyl-3,4-dihydro-2H-pyrrole-2-carboxylate (51.9 mg, 0.2 mmol) in 2 mL of MeOH was added $NaBH_4$ (37.8 mg 1.0 mmol) in portions at 0 °C. The resultant mixture was stirred for 1.5 h at room temperature (monitored by TLC). The mixture was evaporated *in vacuo*, added water (5 mL), and extracted with dichloromethane (5 mL × 3), washed with brine and dried with $MgSO_4$. Concentration and flash chromatography (AcOEt/petroleum ether = 1/1 as eluant) afforded the product **13** (30.8 mg, 0. 118 mmol, 59% yield) as a colorless oil. $[\alpha]^{20}_D$ –45.1 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.23 (d, *J* = 6.0 Hz, 3H), 1.35 (s, 9H), 1.59–1.67 (m, 1H), 2.26–2.33 (m, 1H), 3.15 (s, 1H), 3.21–3.28 (m, 1H), 3.46–3.51 (m, 1H), 3.73 (d, *J* = 7.6 Hz, 1H), 7.18–7.22 (m, 1H), 7.30 (d, *J* = 4.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 142.9, 128.4, 127.5, 126.5, 81.0, 67.6, 54.3, 51.4, 43.9, 27.9, 21.3; MS (ESI) m/z 262.16 $[M + 1]^+$; IR (KBr) ν 3342, 3063, 3029, 2967, 2929, 1725, 1603, 1494, 1456, 1368, 1229, 1160, 1137, 958, 848, 760, 700 cm^{-1}; *er* = 90/10, determined by HPLC analysis (Chiralpak AD-H, *n*-hexane/2-propanol = 95/5, 1.0 ml/min, 254 nm UV detector), t_R = 8.4 min (major) and t_R = 9.7 min (minor).

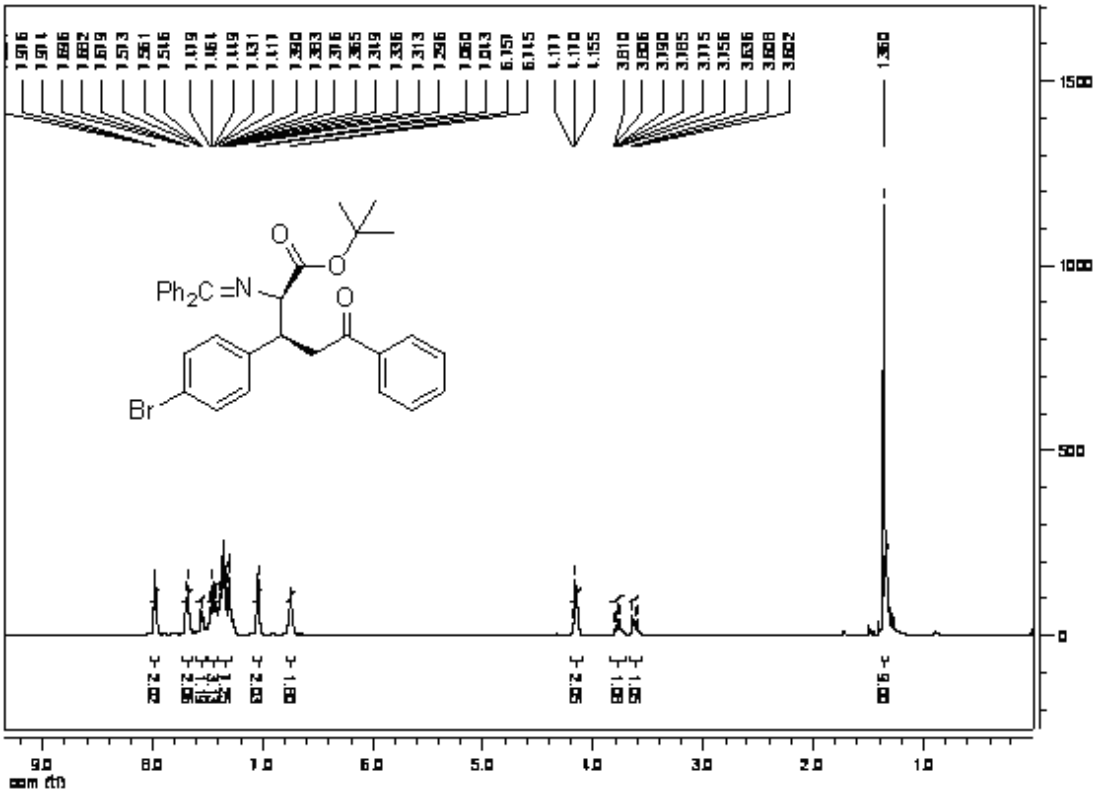
7. References:

1. a) M.-Q. Hua, H.-F. Cui, L. Wang, J. Nie, J.-A. Ma, *Angew. Chem., Int. Ed.* 2010, **49**, 2772.
   b) T. Ooi, M. Kameda, K. Maruoka, *J. Am. Chem. Soc.* 2003, **125**, 5139.
   c) T. Ooi, K. Maruoka, *Angew. Chem. Int. Ed.* 2007, **46**, 4222.
   d) T. Hashimoto, K. Maruoka, *Chem. Rev*. 2007, **107**, 5656.
2. a) R. Viswanathan, E. N. Prabhakaran, M. A. Plotkin, J. N. Johnston, *J. Am. Chem. Soc.* 2003, **125**, 163.
   b) R. Viswanathan, C. R. Smith, E. N. Prabhakaran, J. N. Johnston, *J. Org. Chem.* 2008, **73**, 3040.

8. NMR Spectra and HPLC Charts for the Addition Adducts



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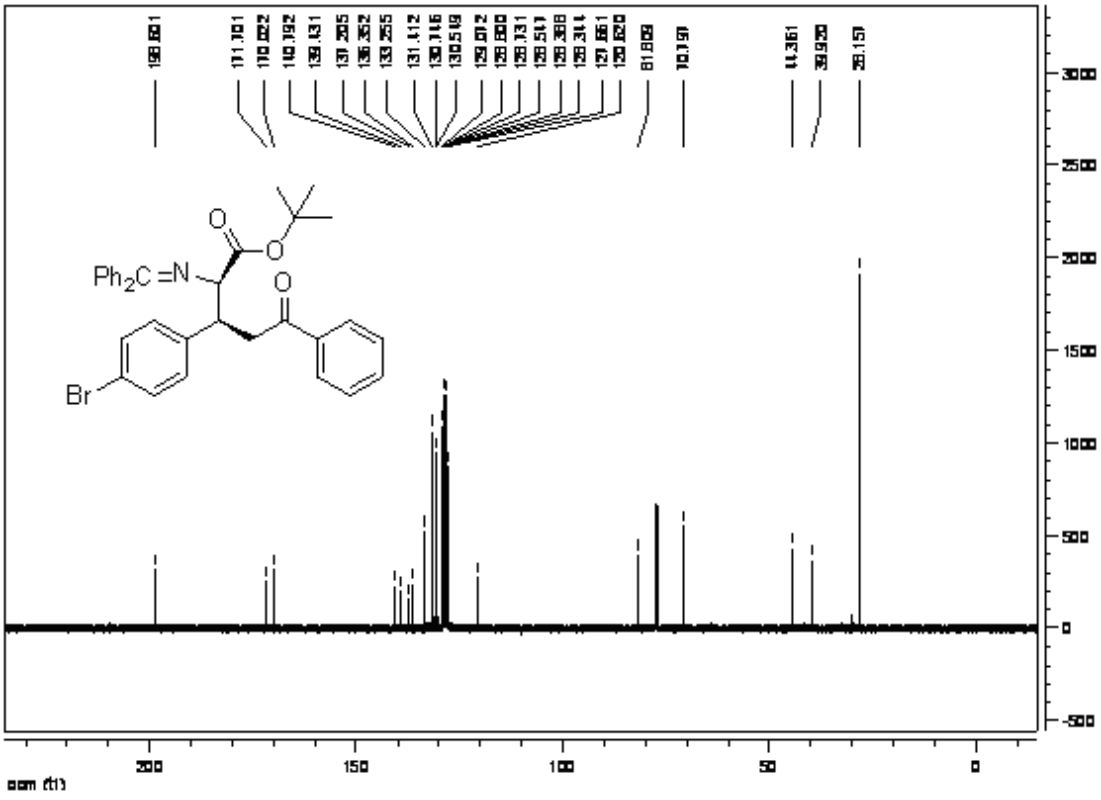
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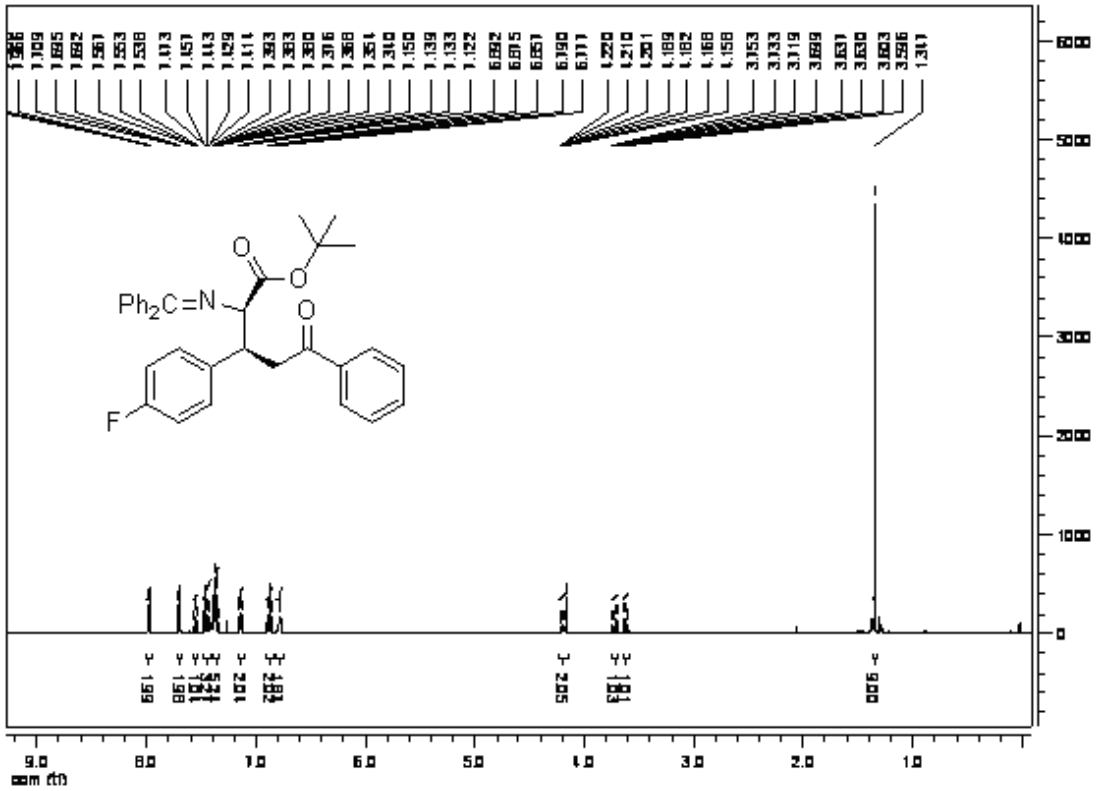
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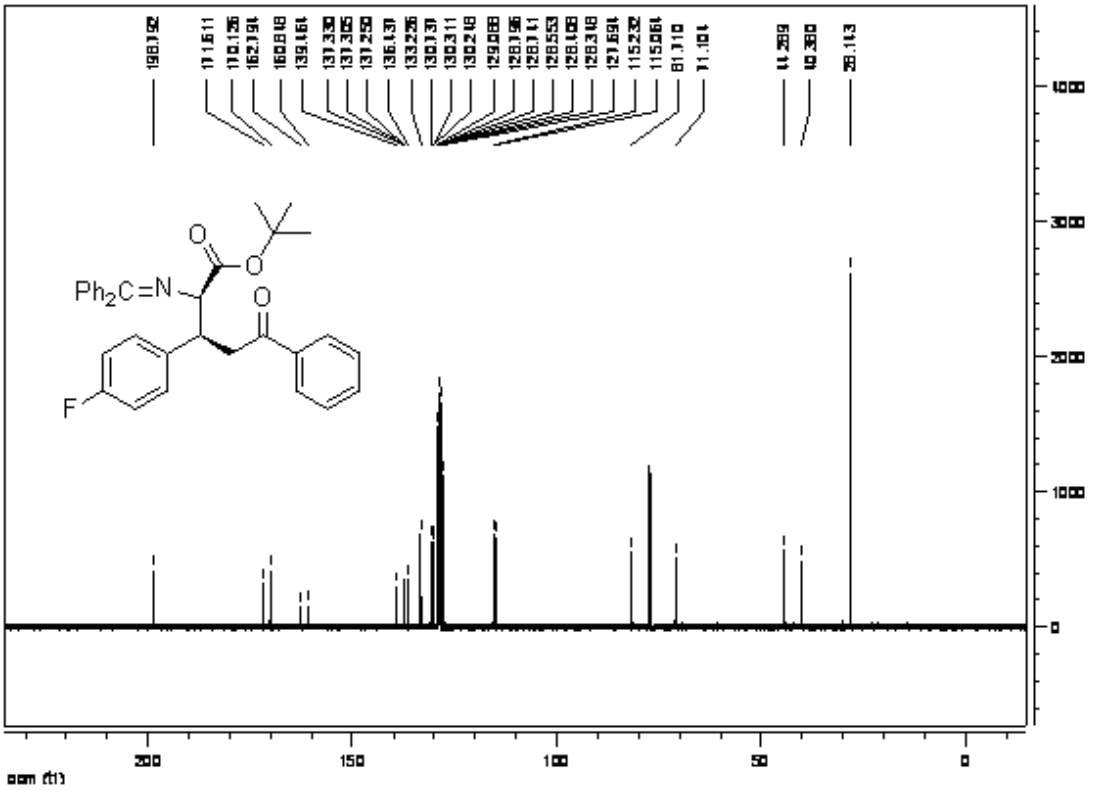
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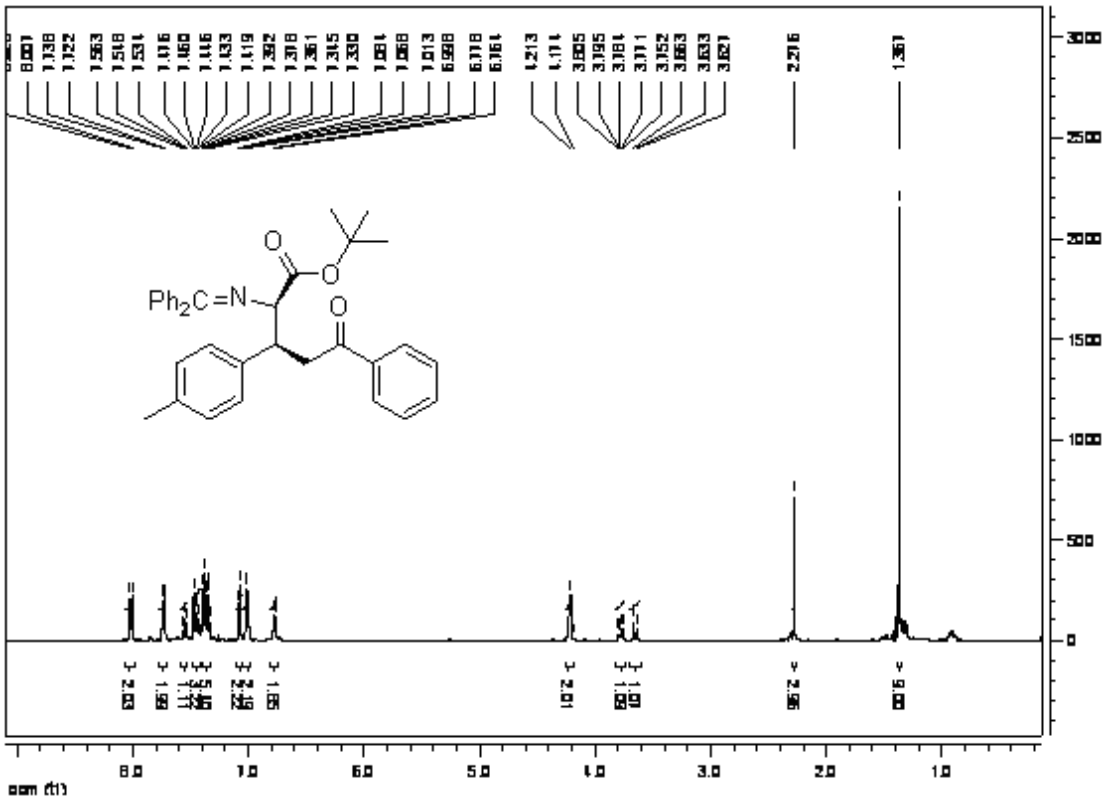
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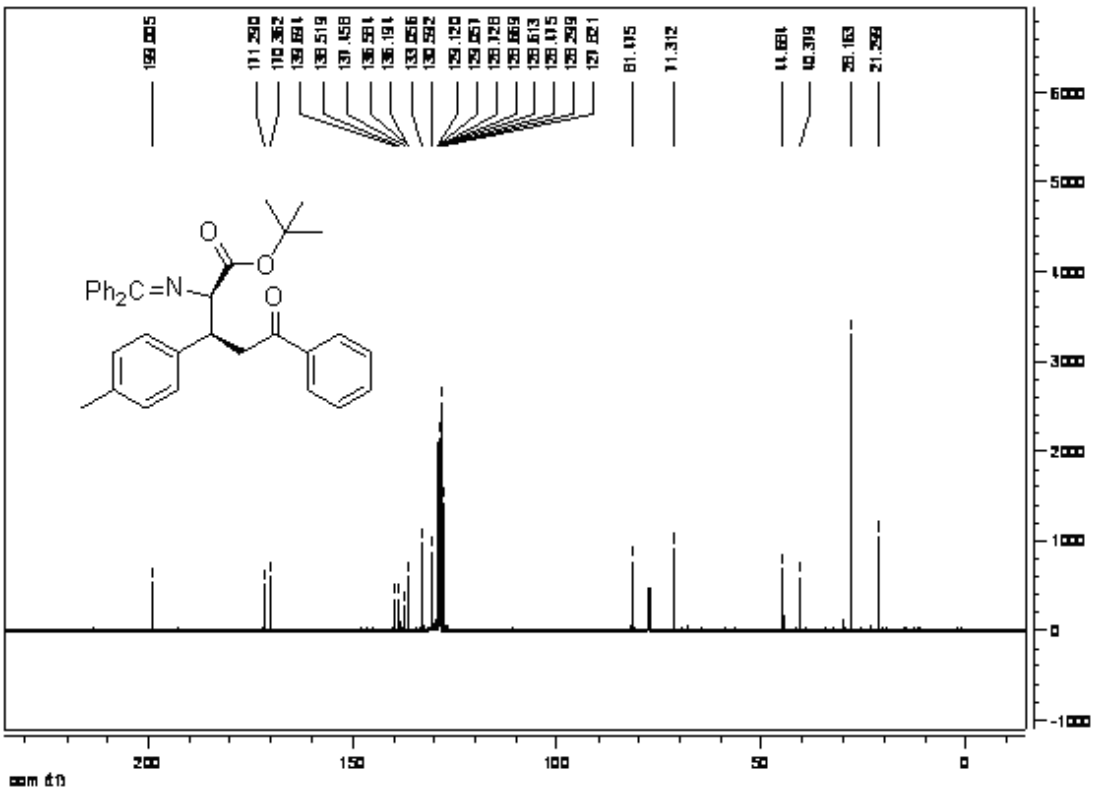
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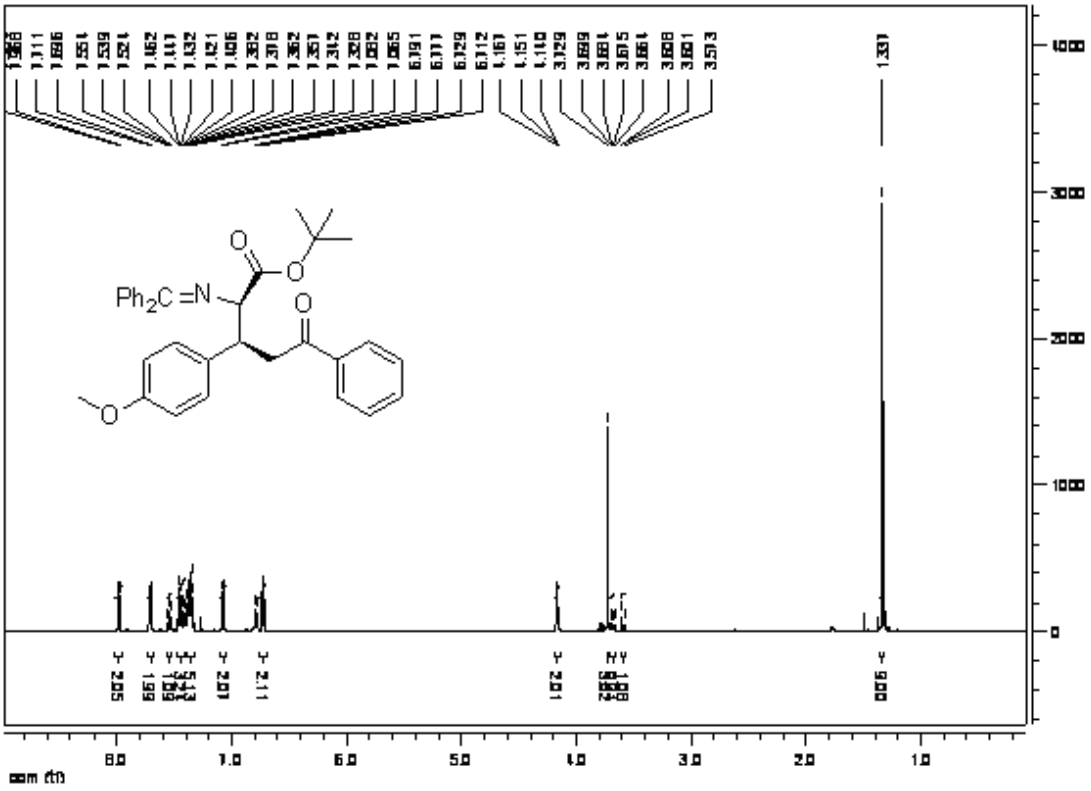
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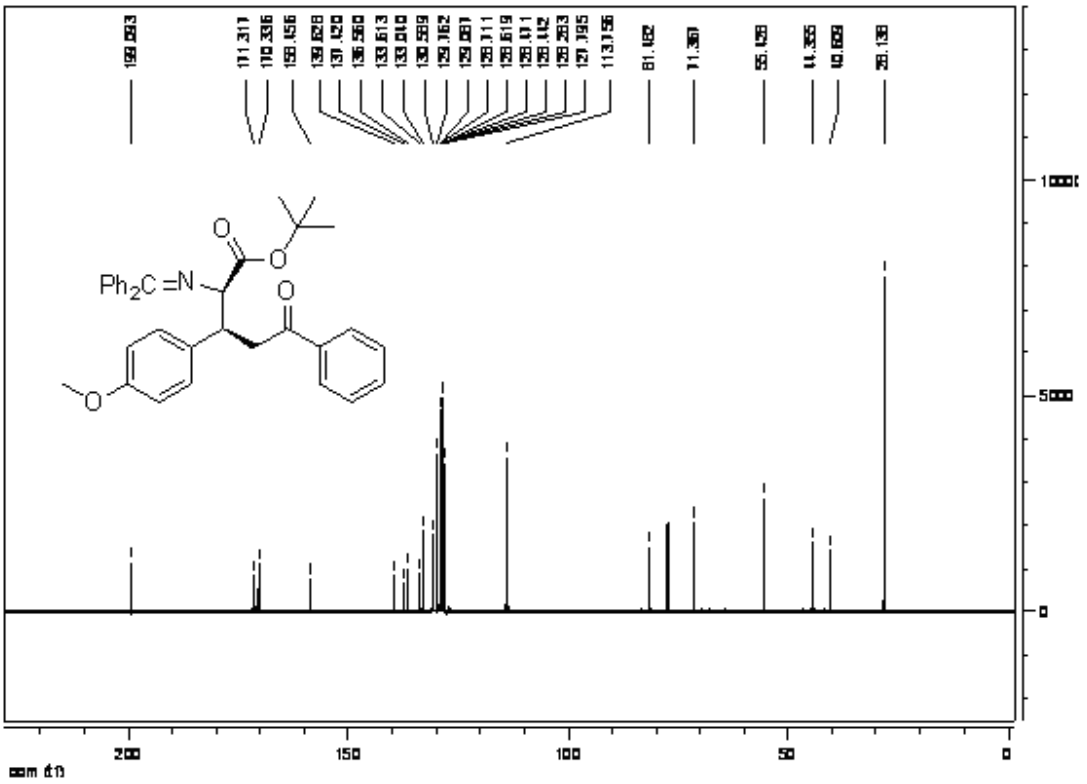
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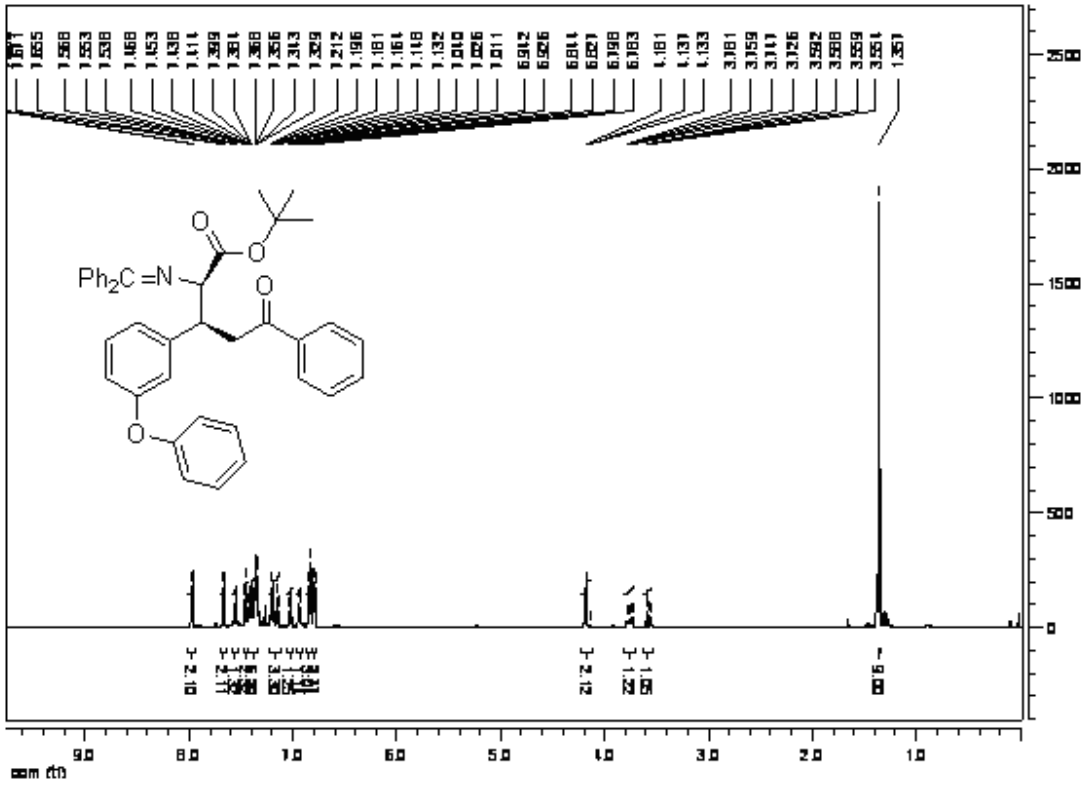
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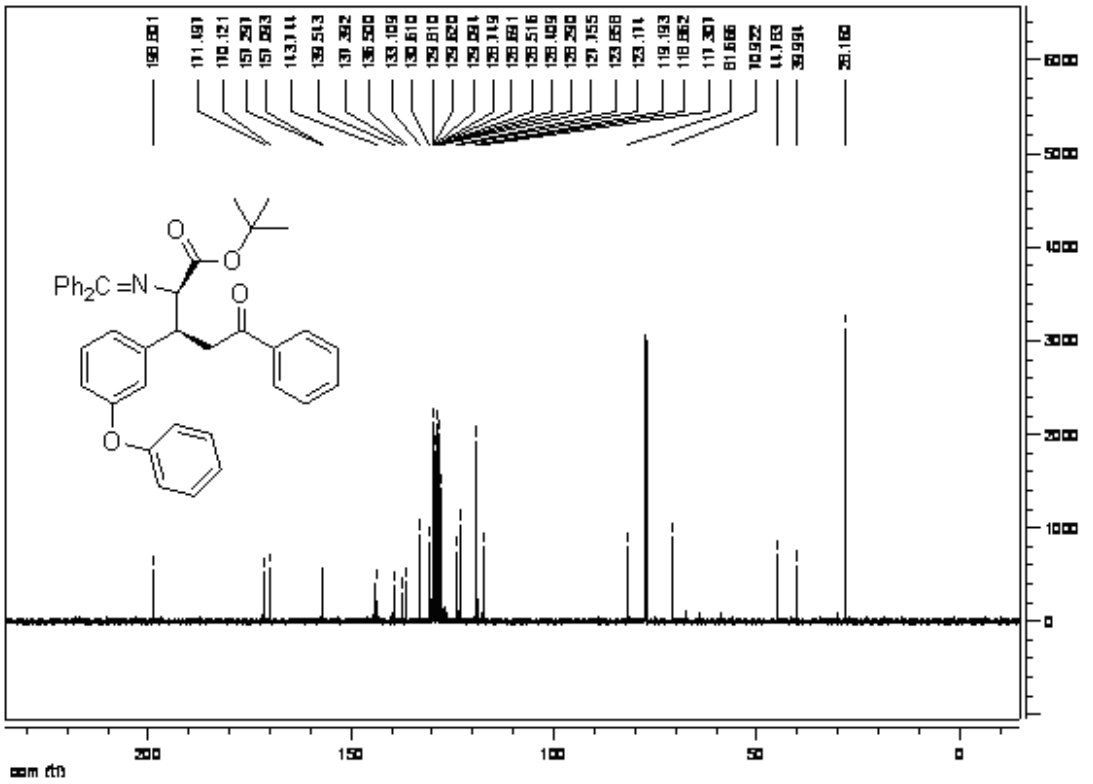
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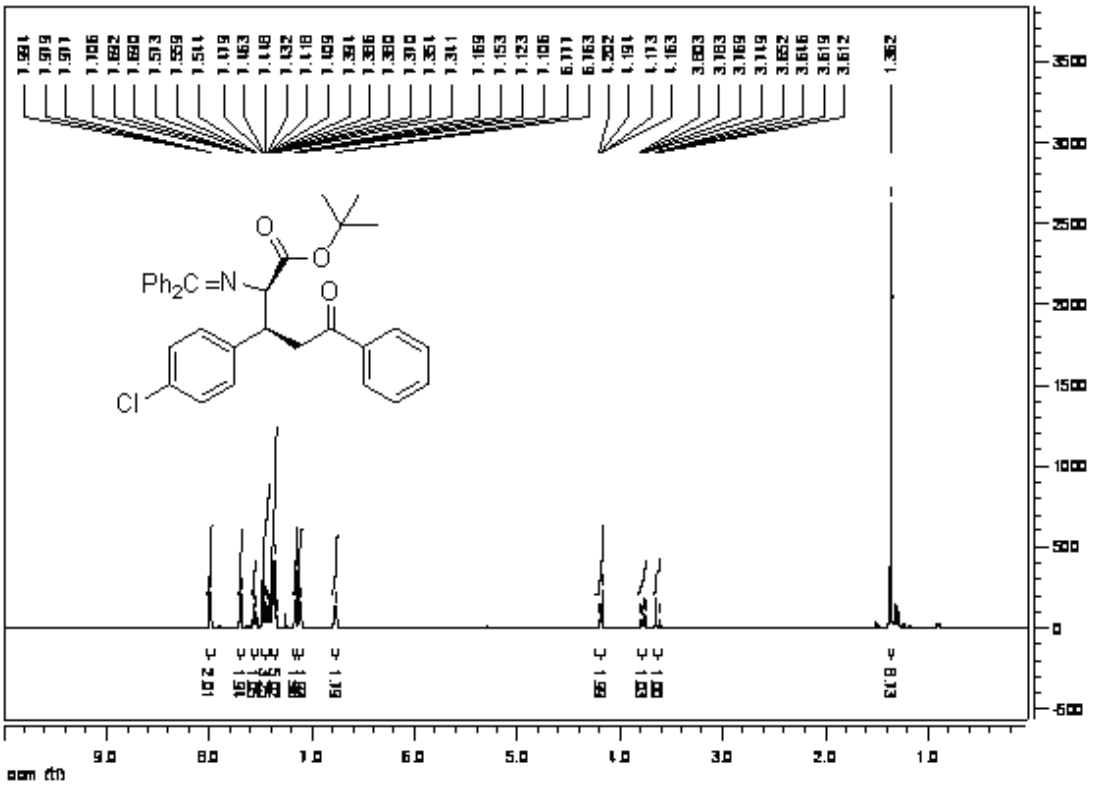
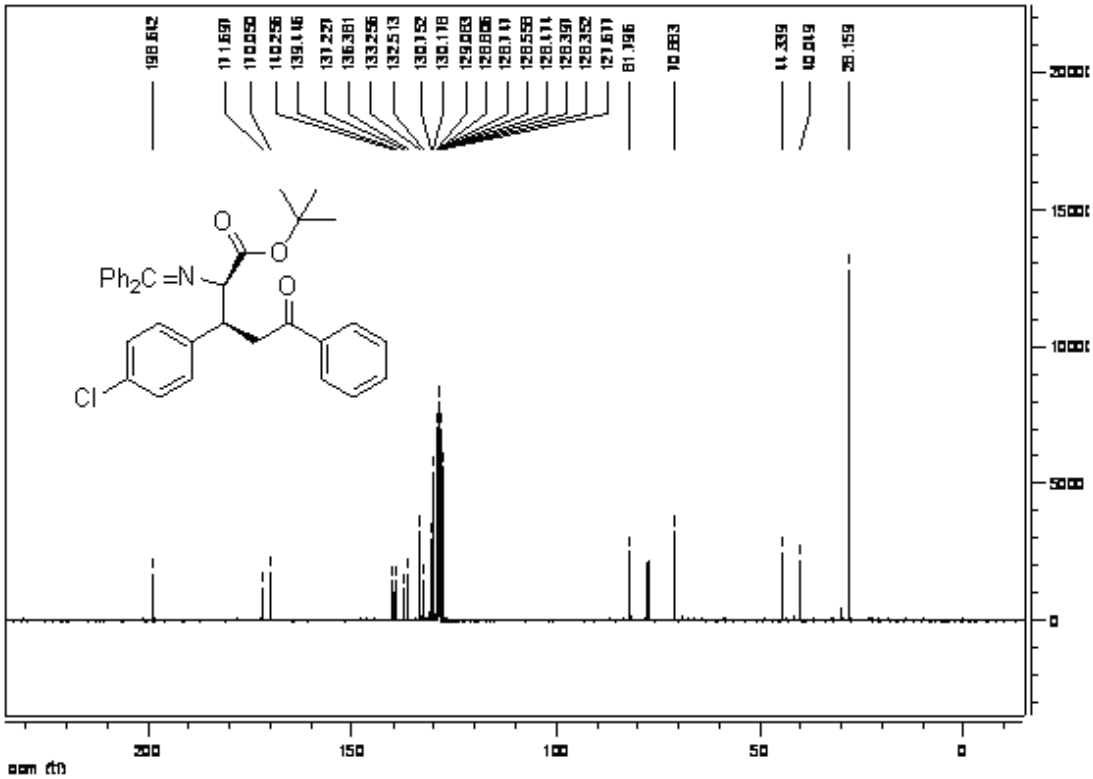
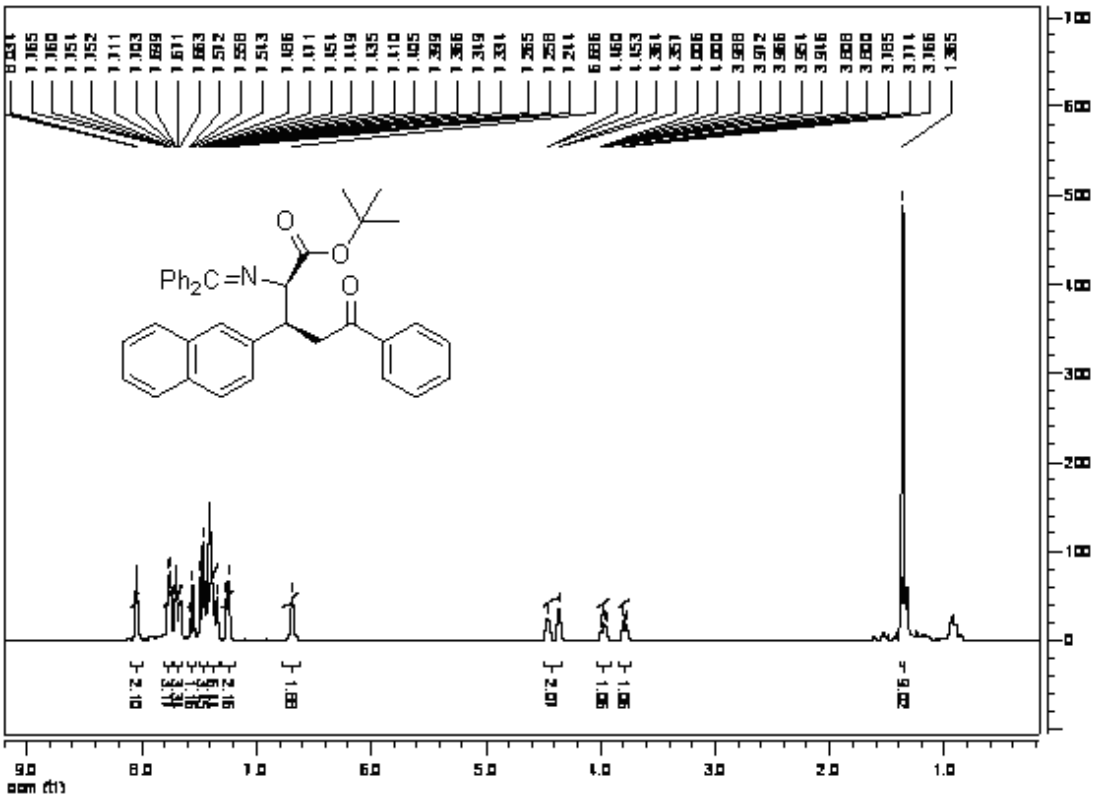
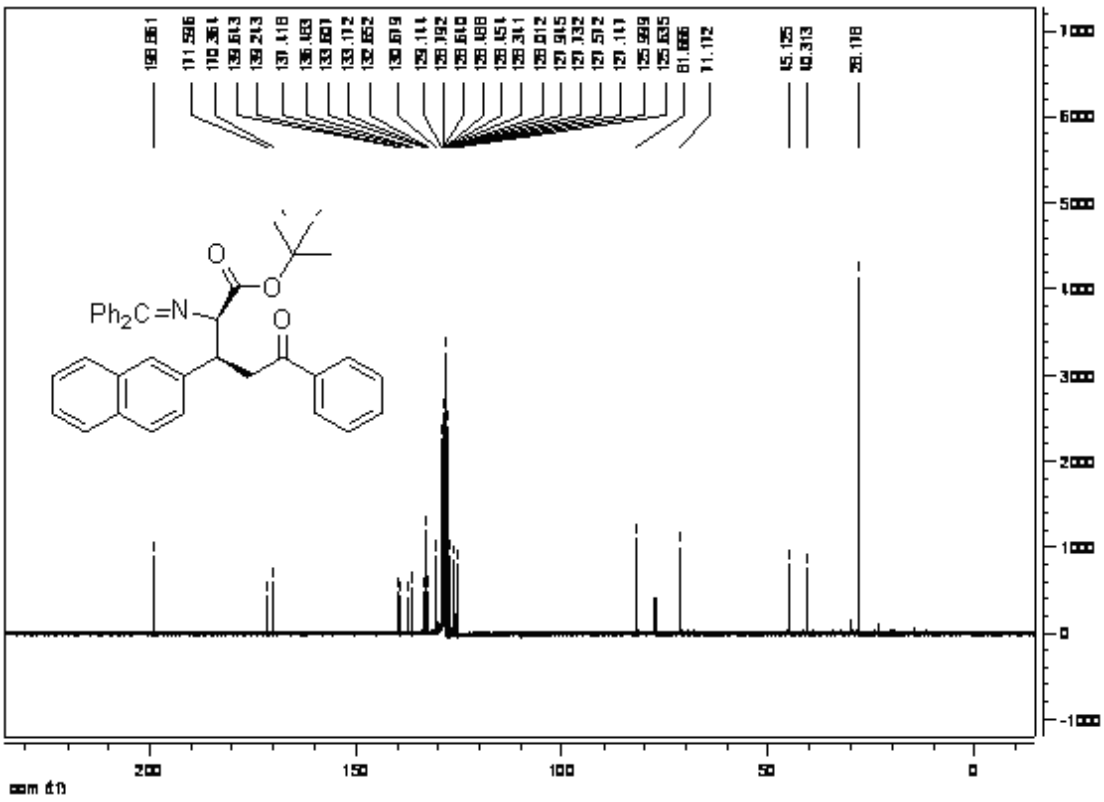
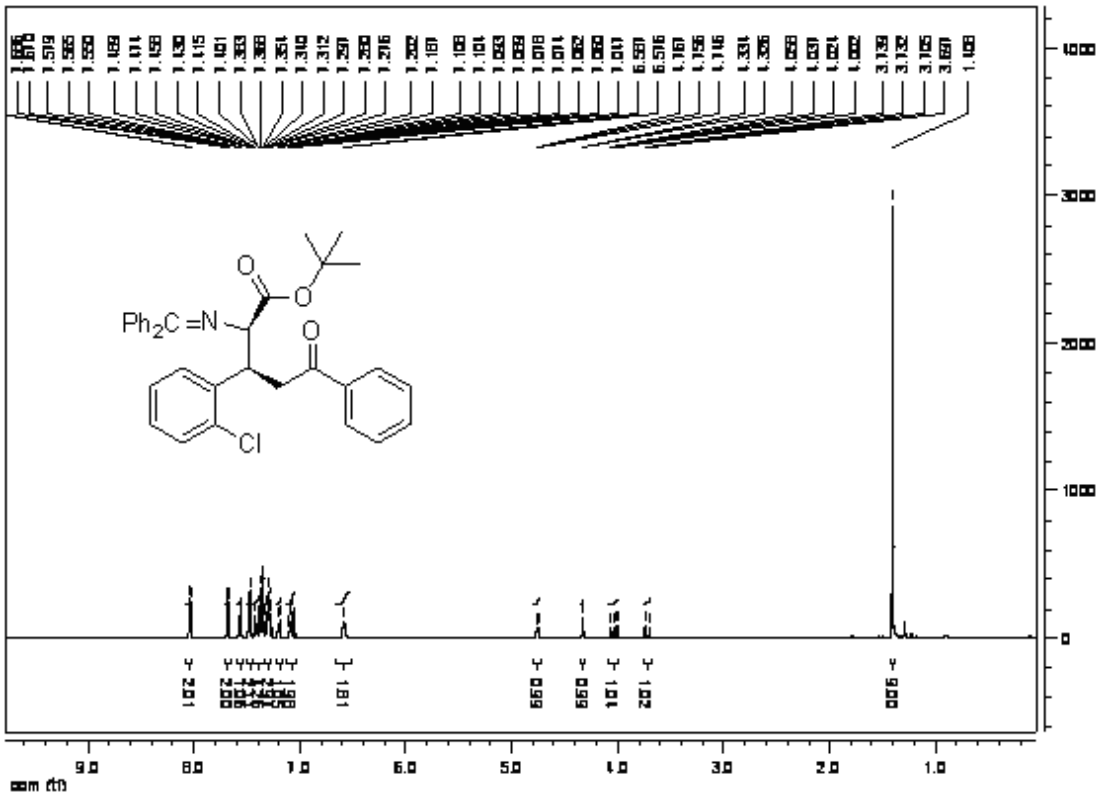
O
ppm (f1)

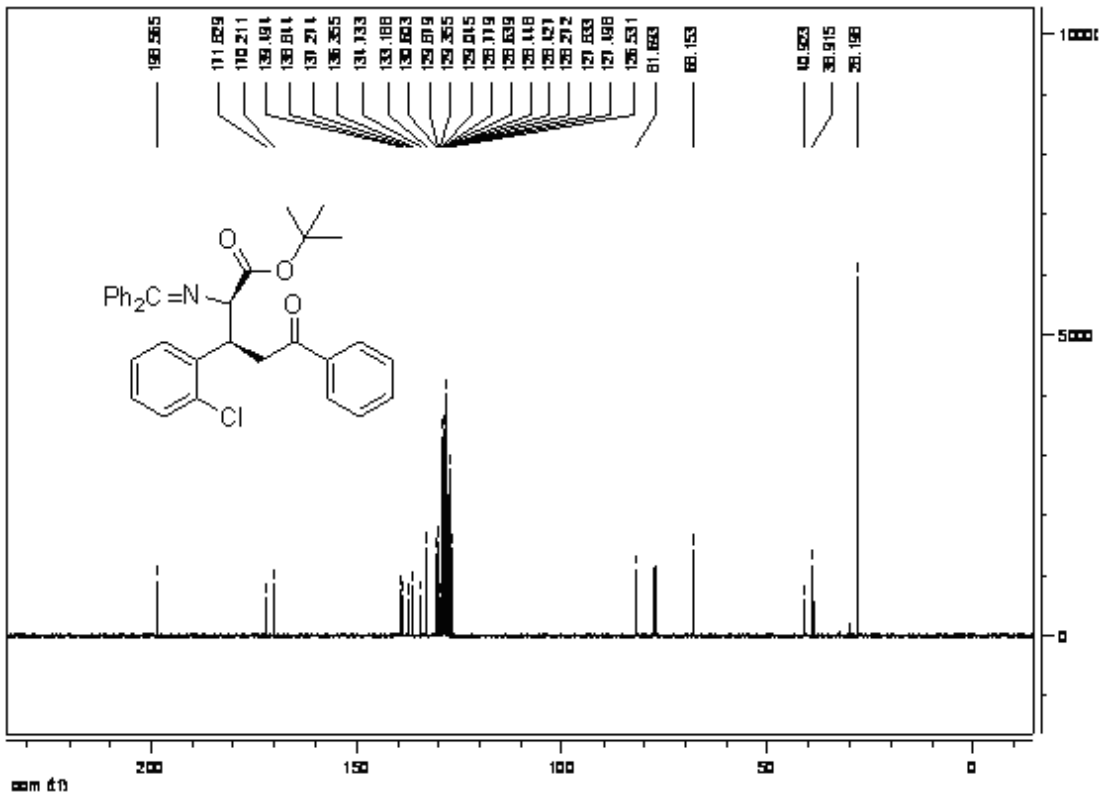

Ph2C =N
O
O
O
Cl
ppm (f1)

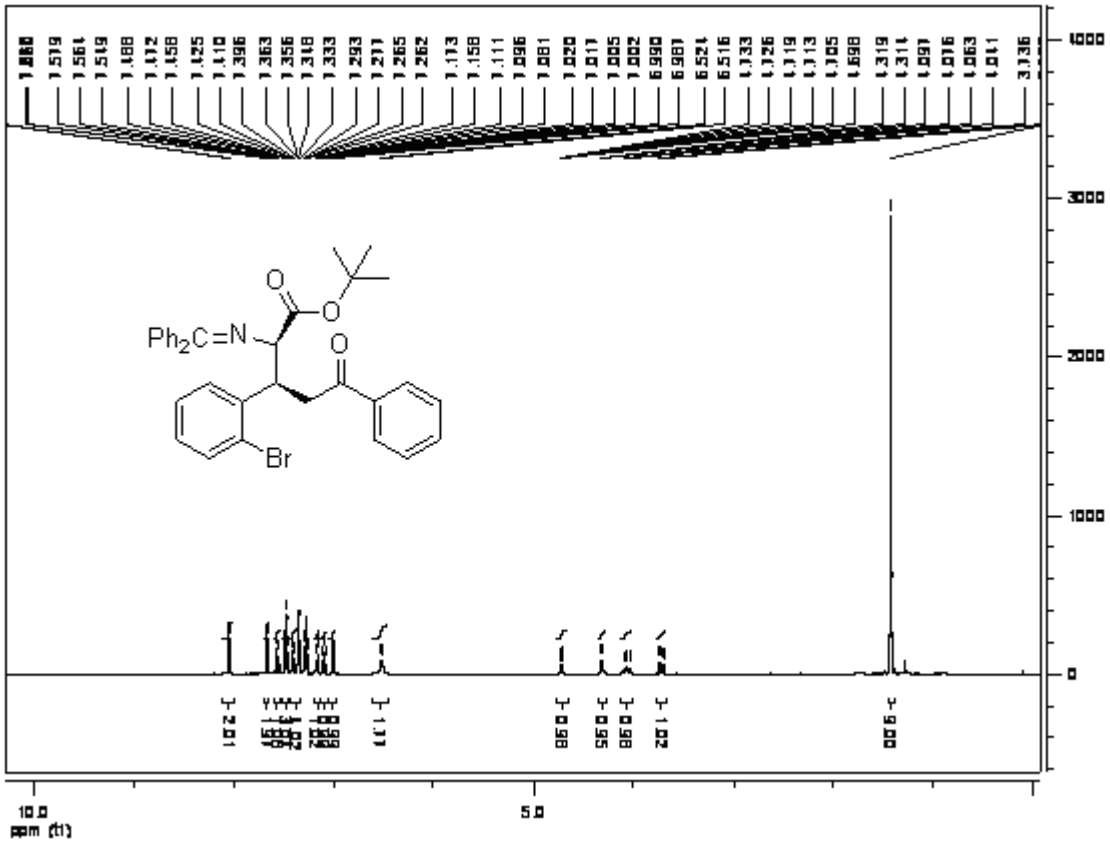

Ph2C =N
O
O
O
Cl
ppm (f1)

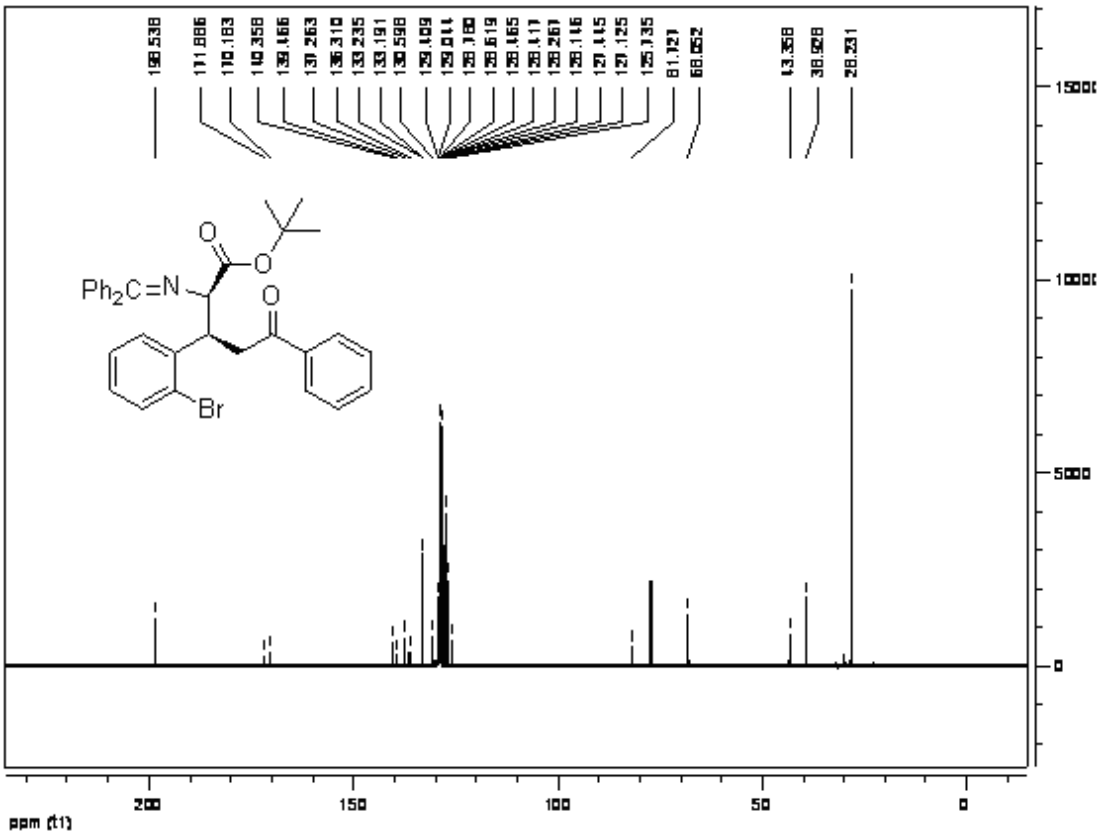

Ph2C=N
O
O
O
ppm (t1)

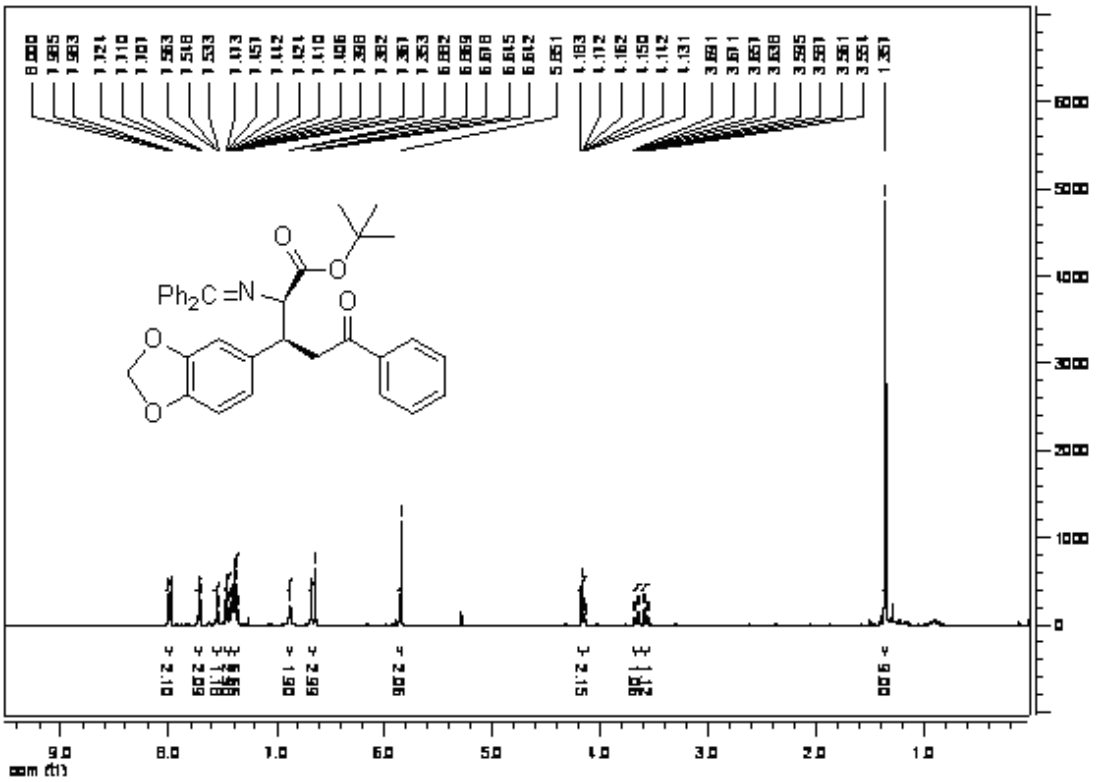

Ph2C=N
O
O
O
ppm (t1)

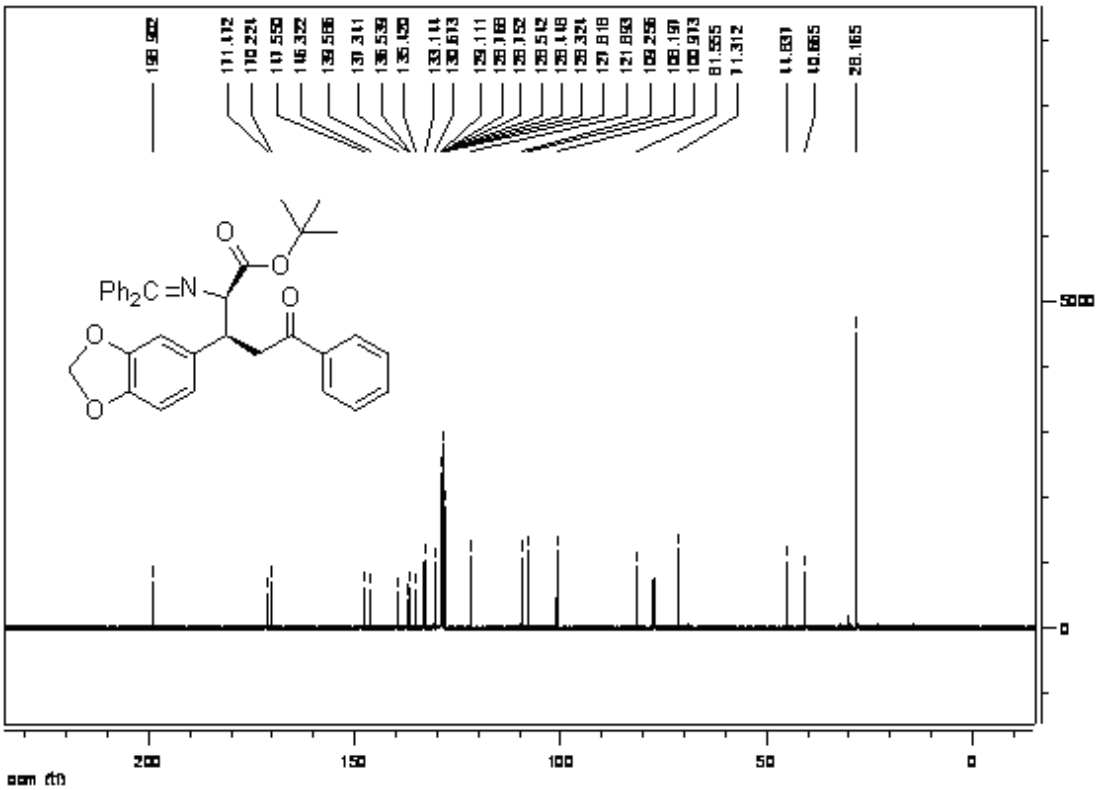

Ph2C =N
O
O
O
Cl

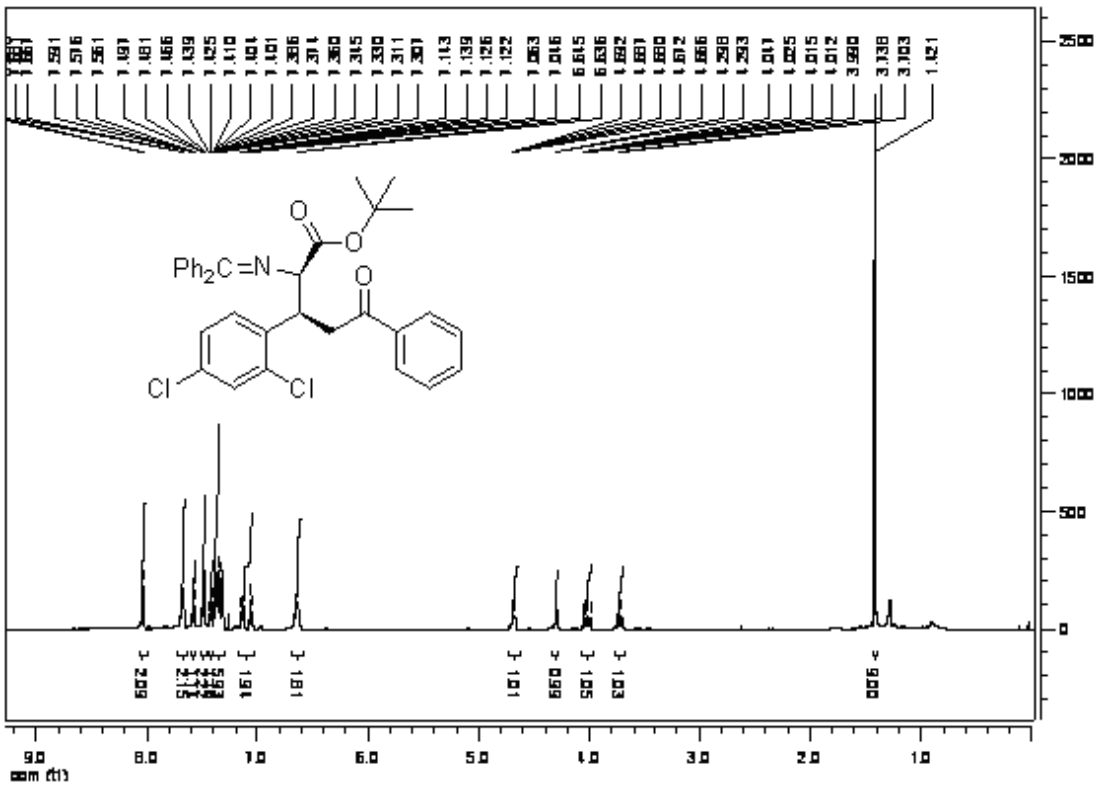

Ph2C =N
O
O
O
Cl

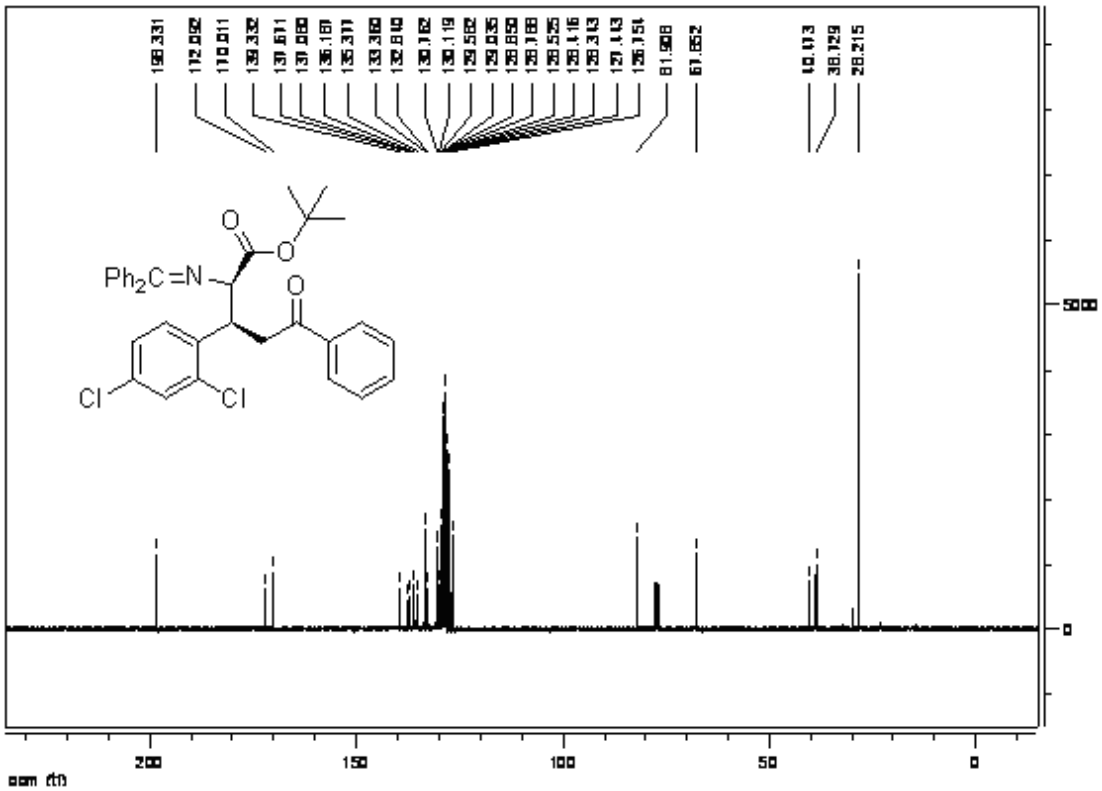

Ph2C=N
O
O
O
Br
10.0
5.0
ppm (t1)

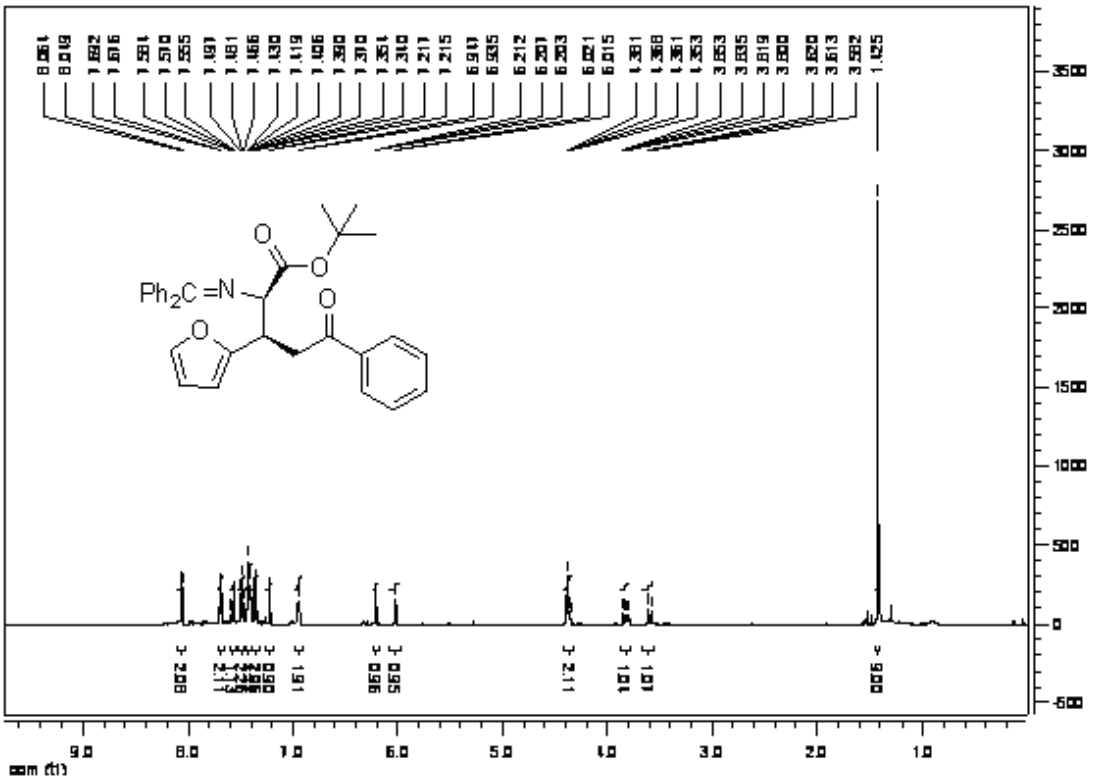

Ph2C=N
O
O
O
Br
200
150
100
50
0
ppm (t1)

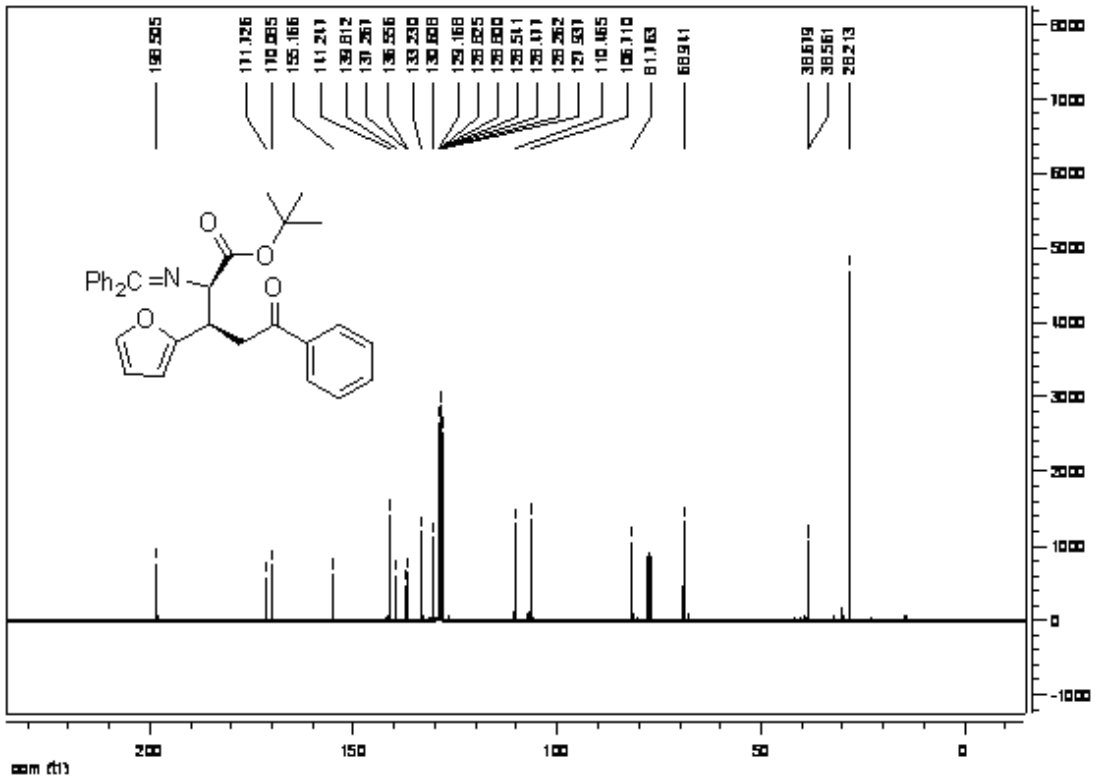

Ph2C =N
O
O
O
O
O
ppm (t1)

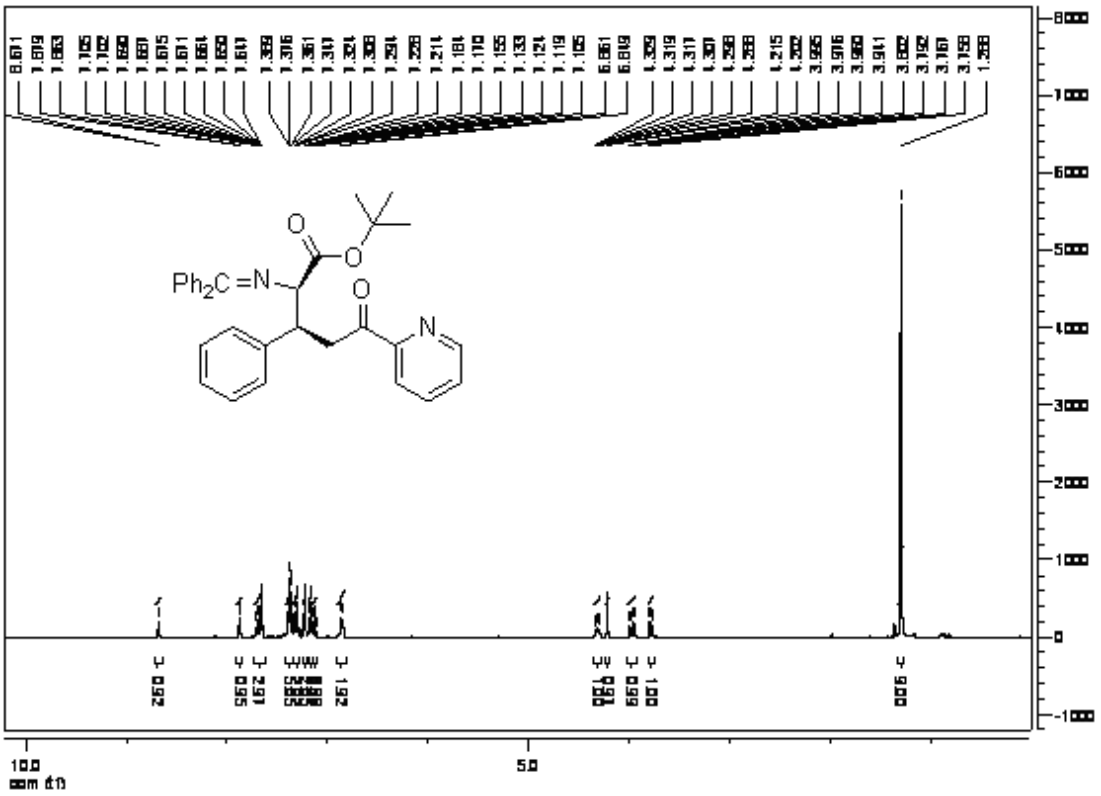

Ph2C =N
O
O
O
O
O
ppm (t1)

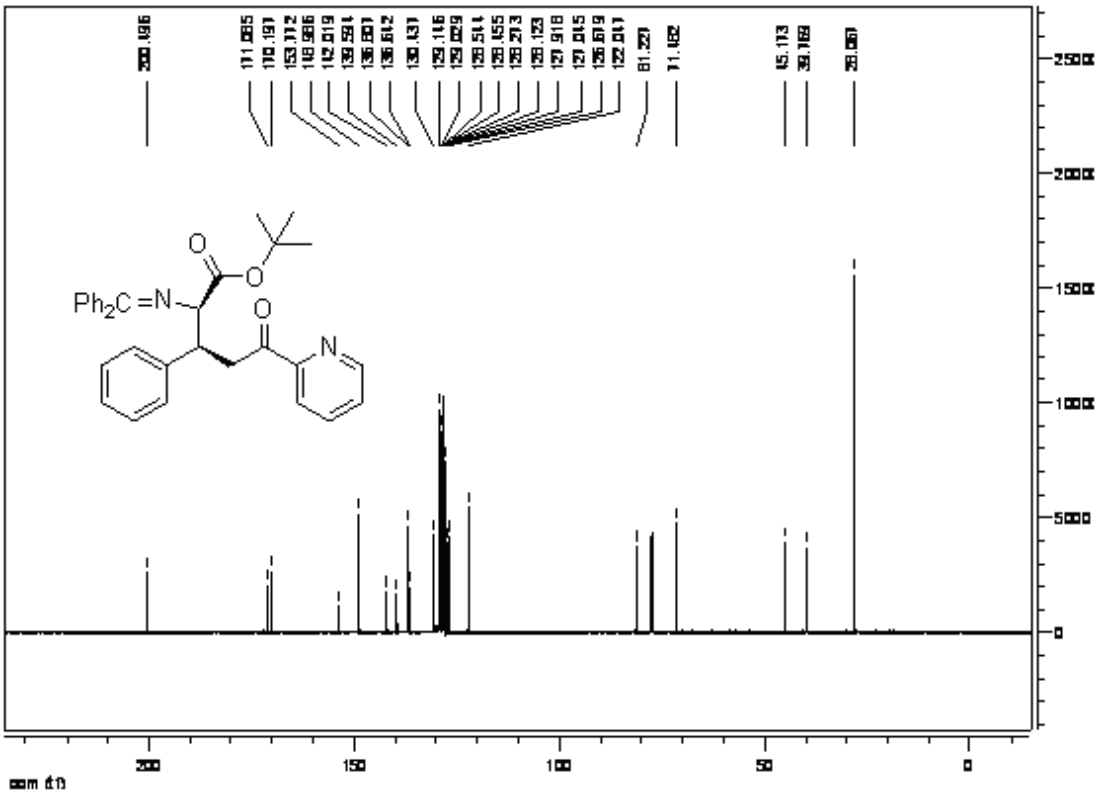

Ph2C=N
O
O
O
Cl
Cl

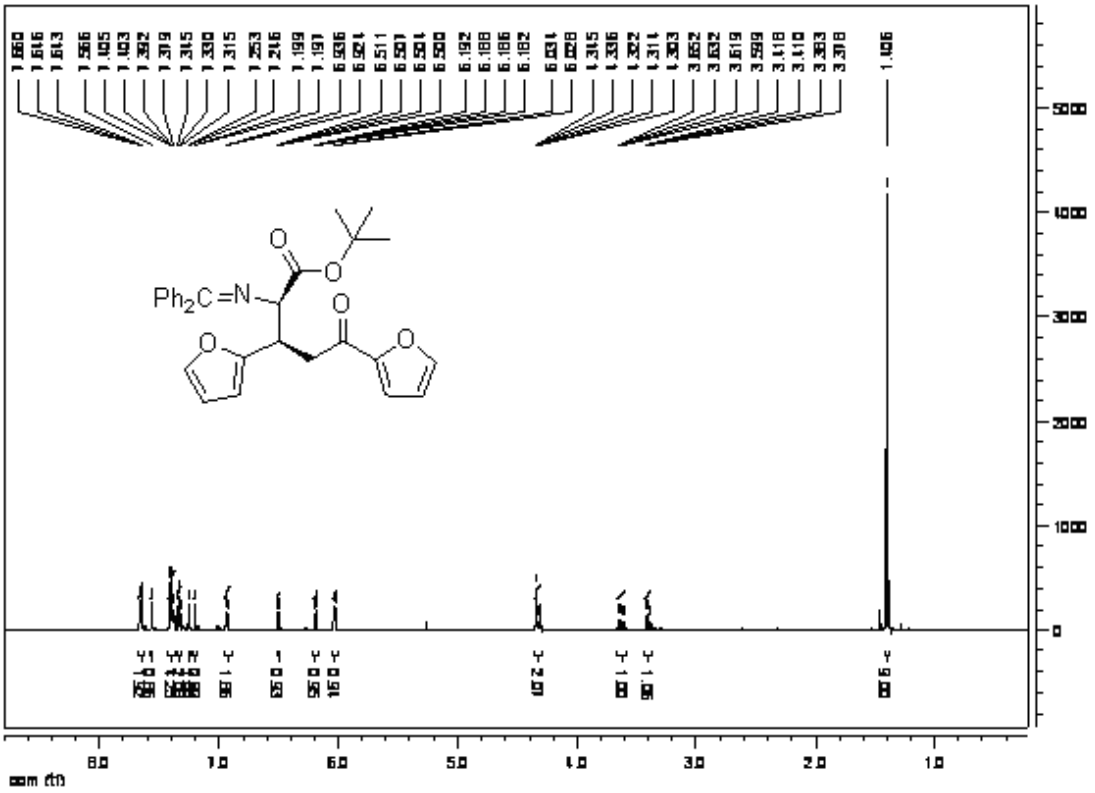

Ph2C=N
O
O
O
Cl
Cl

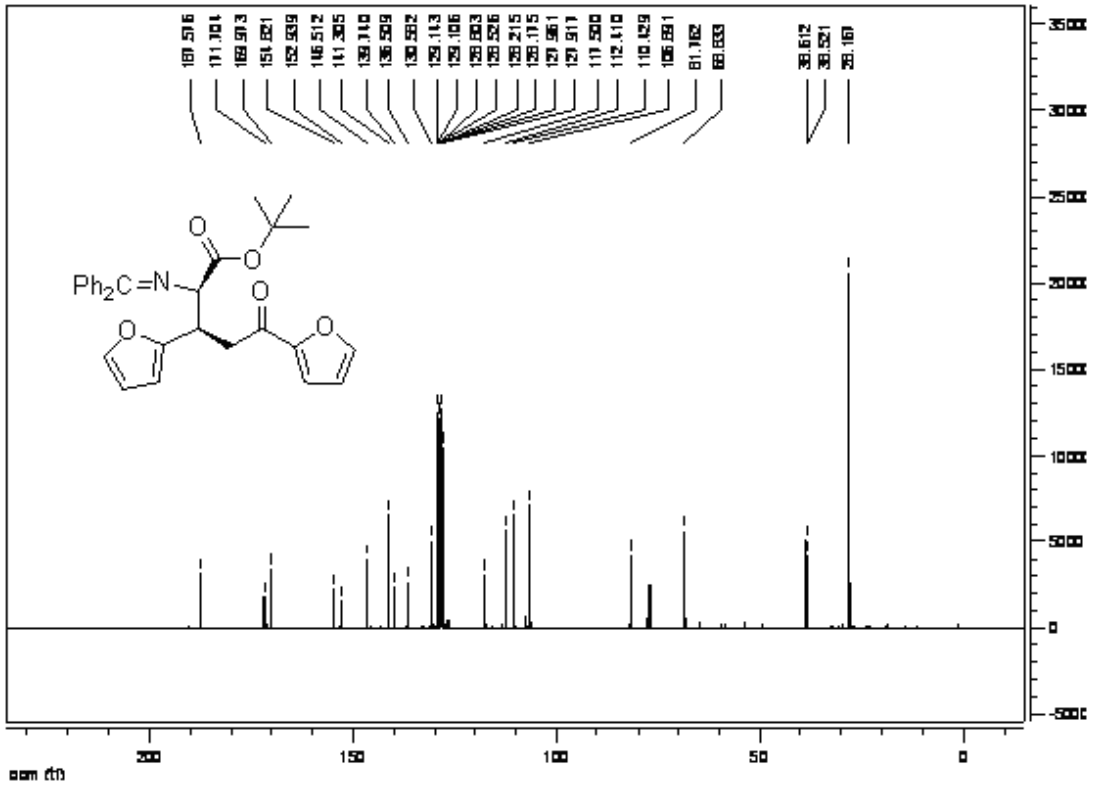

Ph2C =N
O
O
O
O

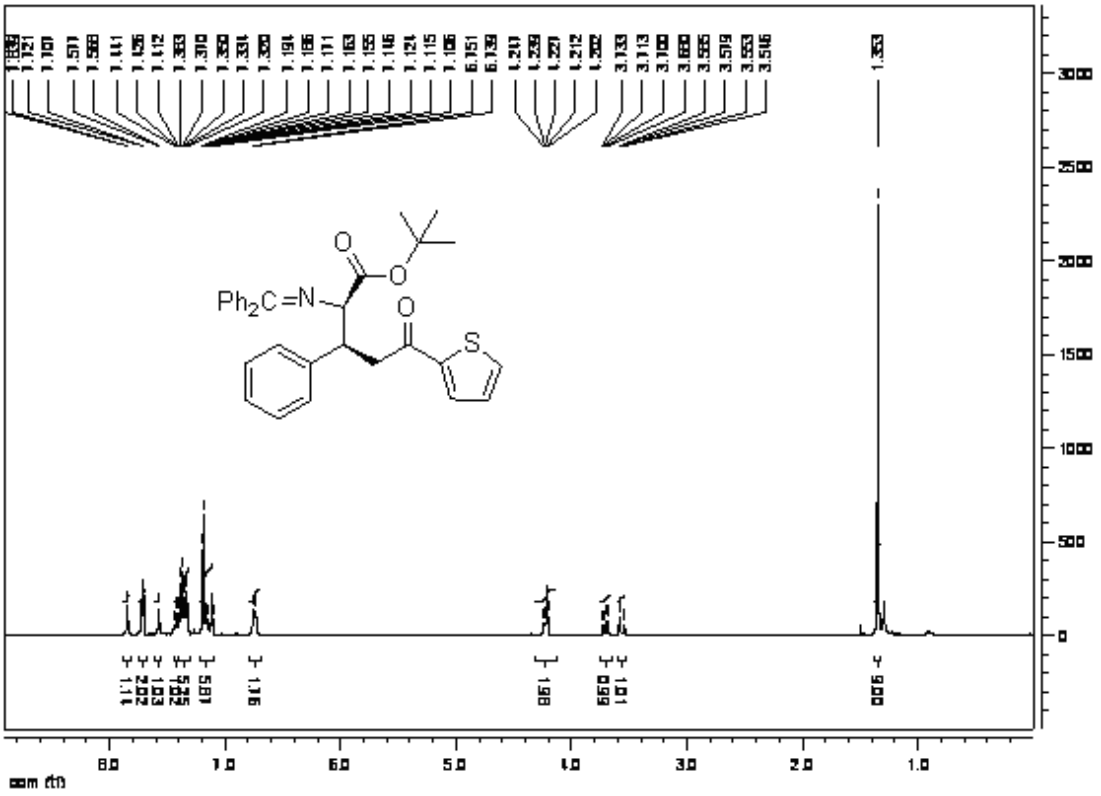

Ph2C =N
O
O
O
O

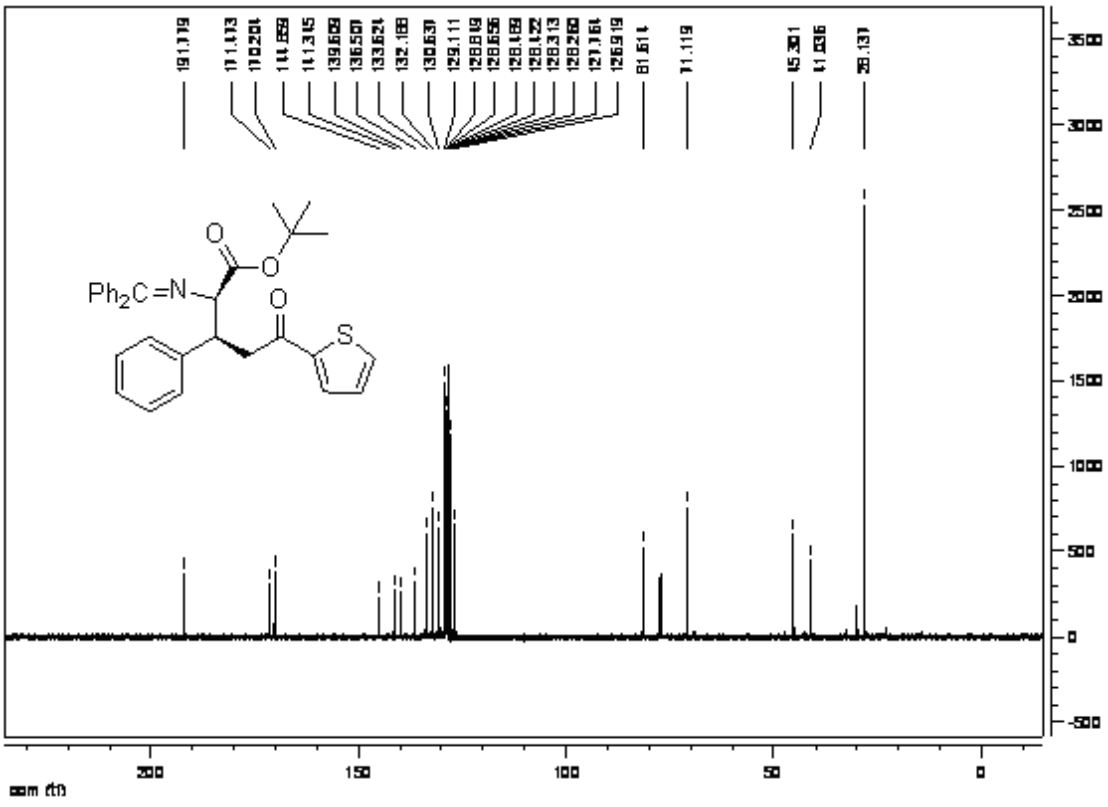


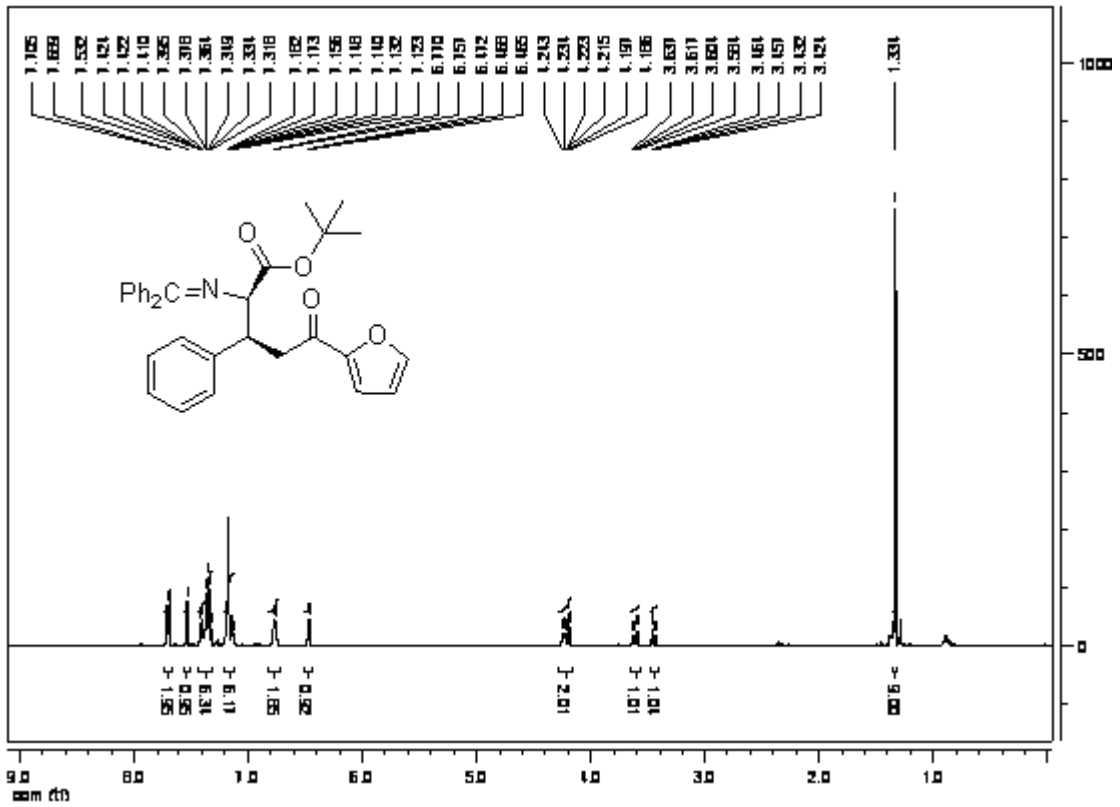


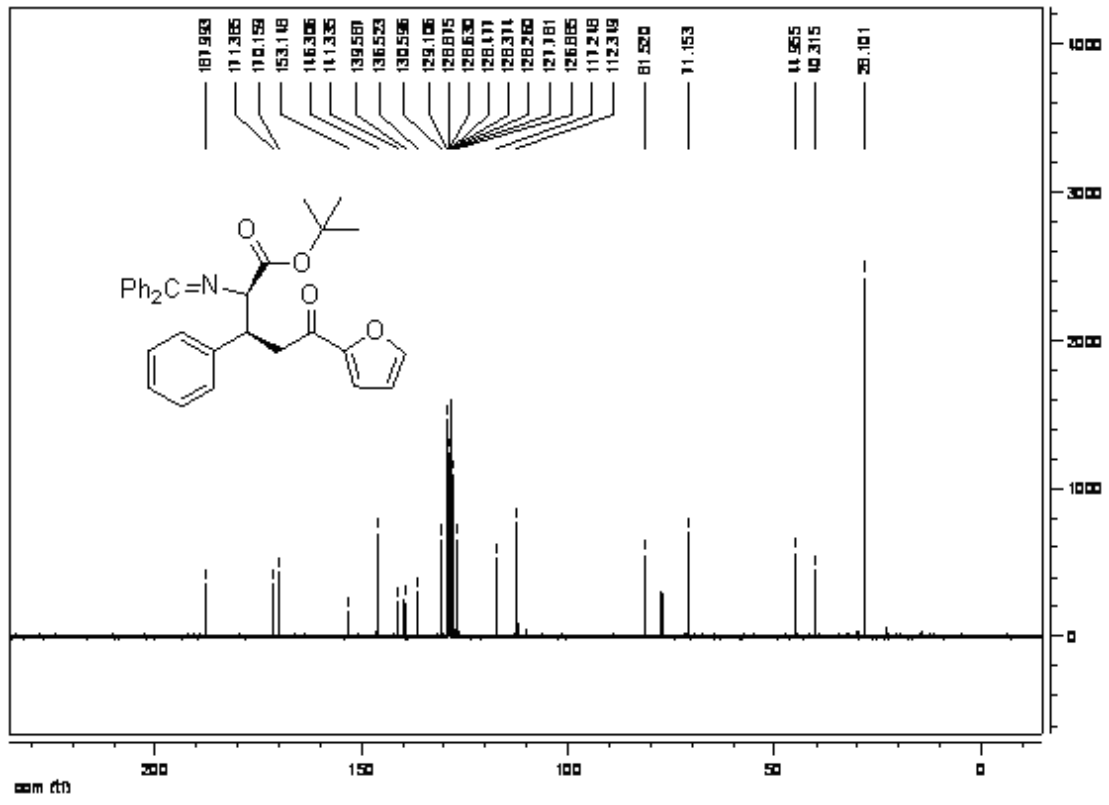

Ph2C=N
O
O
O
O
O

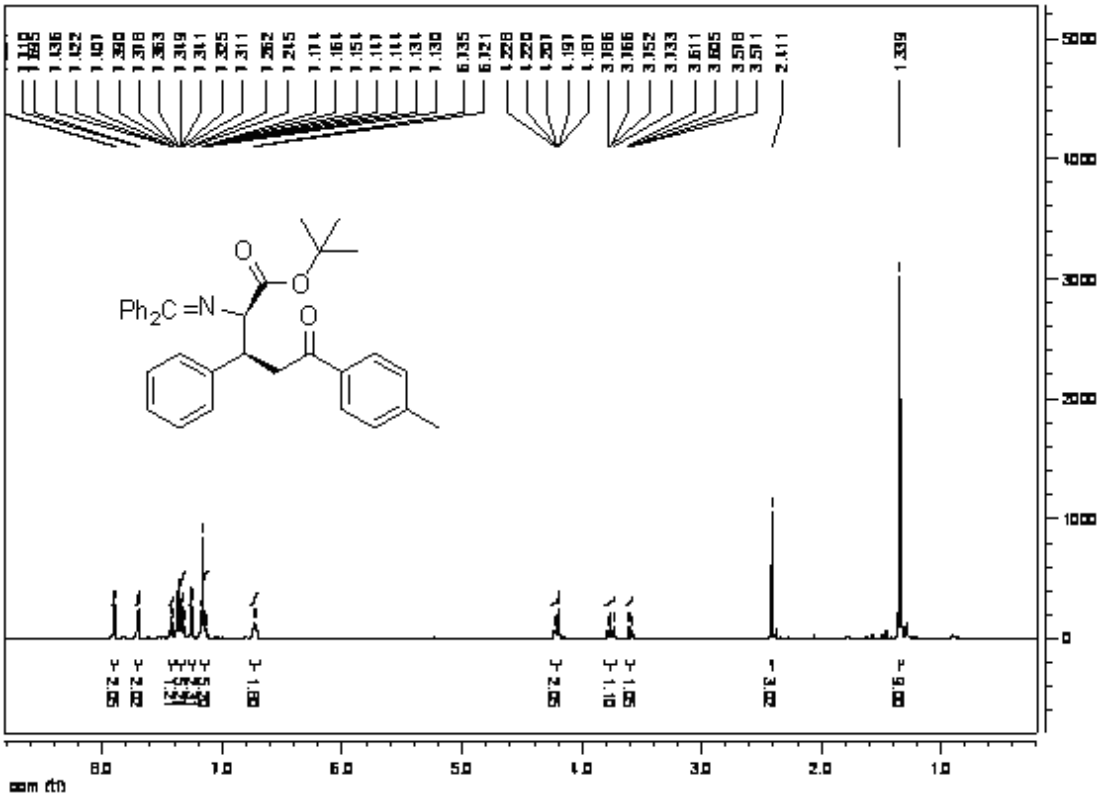

Ph2C=N
O
O
O
O
O

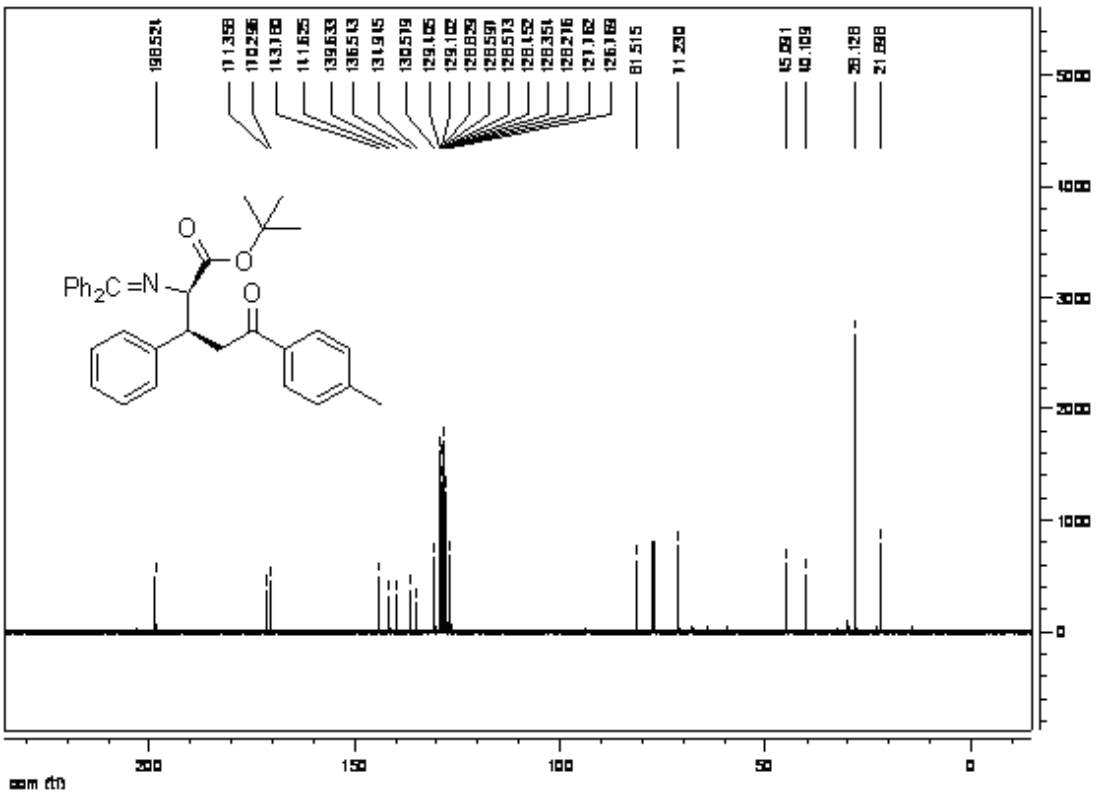

Ph2C=N
O
O
O
S

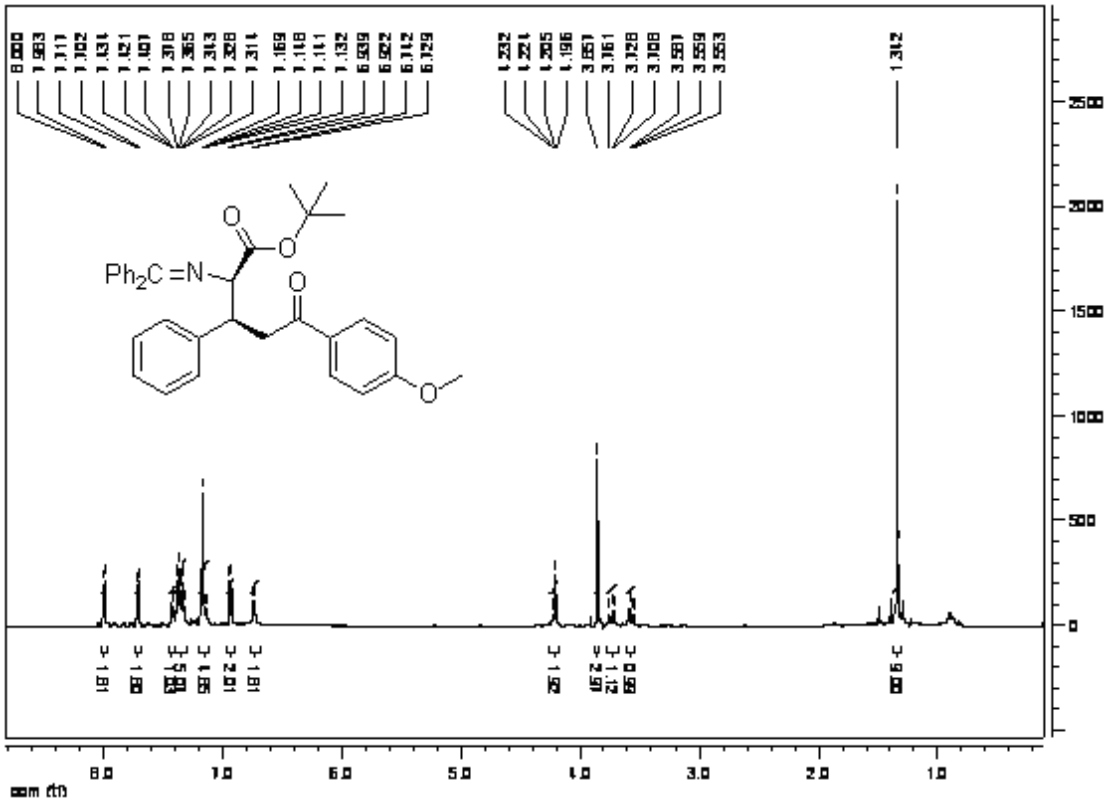

Ph2C=N
O
O
O
S

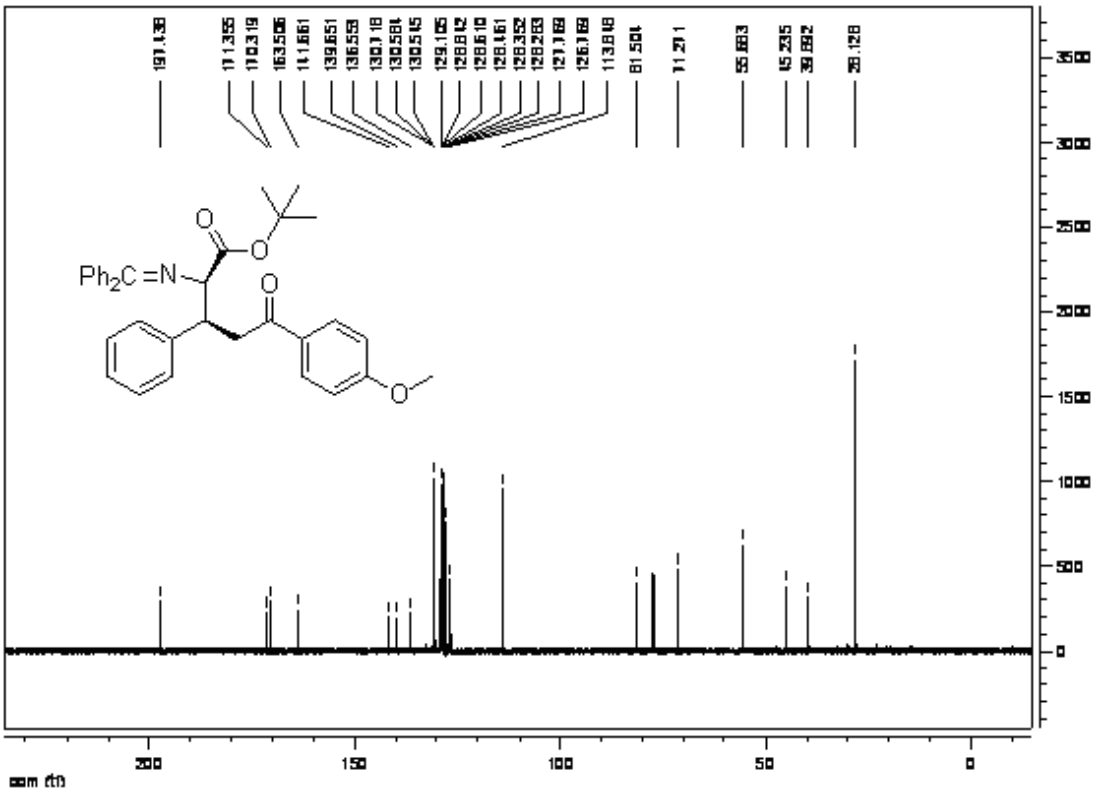

Ph2C=N
O
O
O
O
ppm (f1)

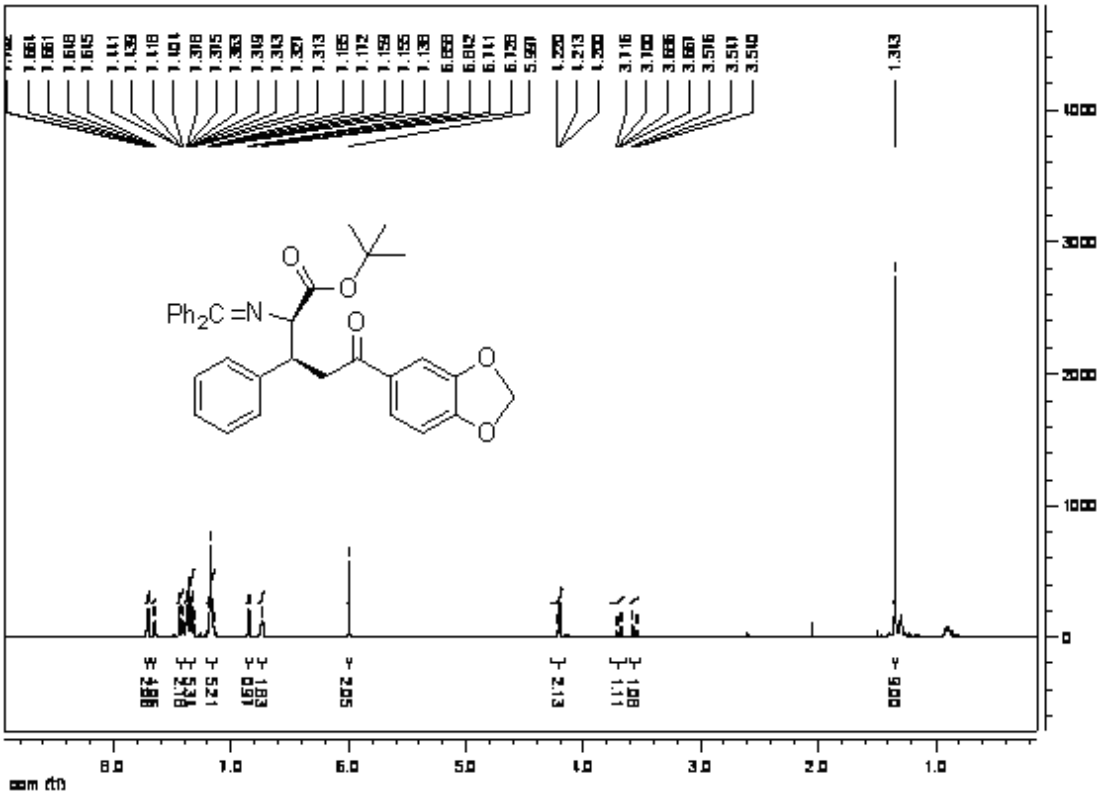

Ph2C=N
O
O
O
O
ppm (f1)

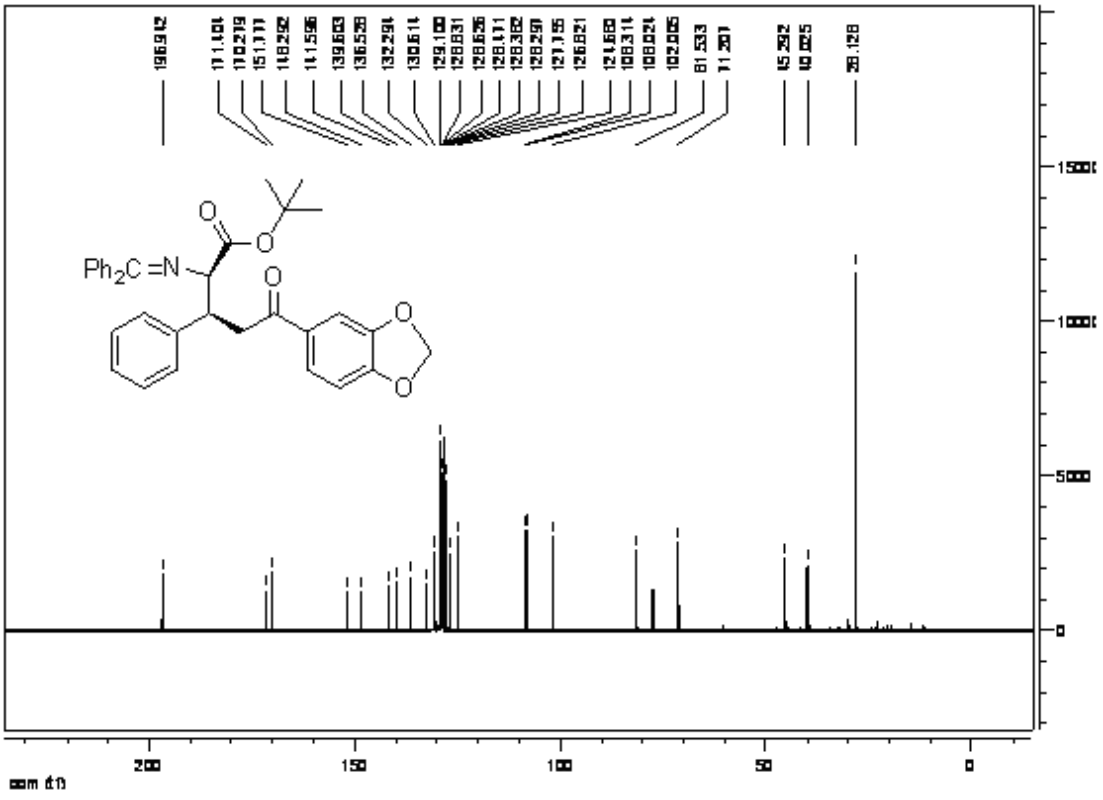

Ph2C =N
O
O
O
1.339
2.411
3.501
3.508
3.605
3.611
3.733
3.752
3.766
3.986
4.181
4.191
4.201
4.220
4.228
6.121
6.135
ppm (f1)

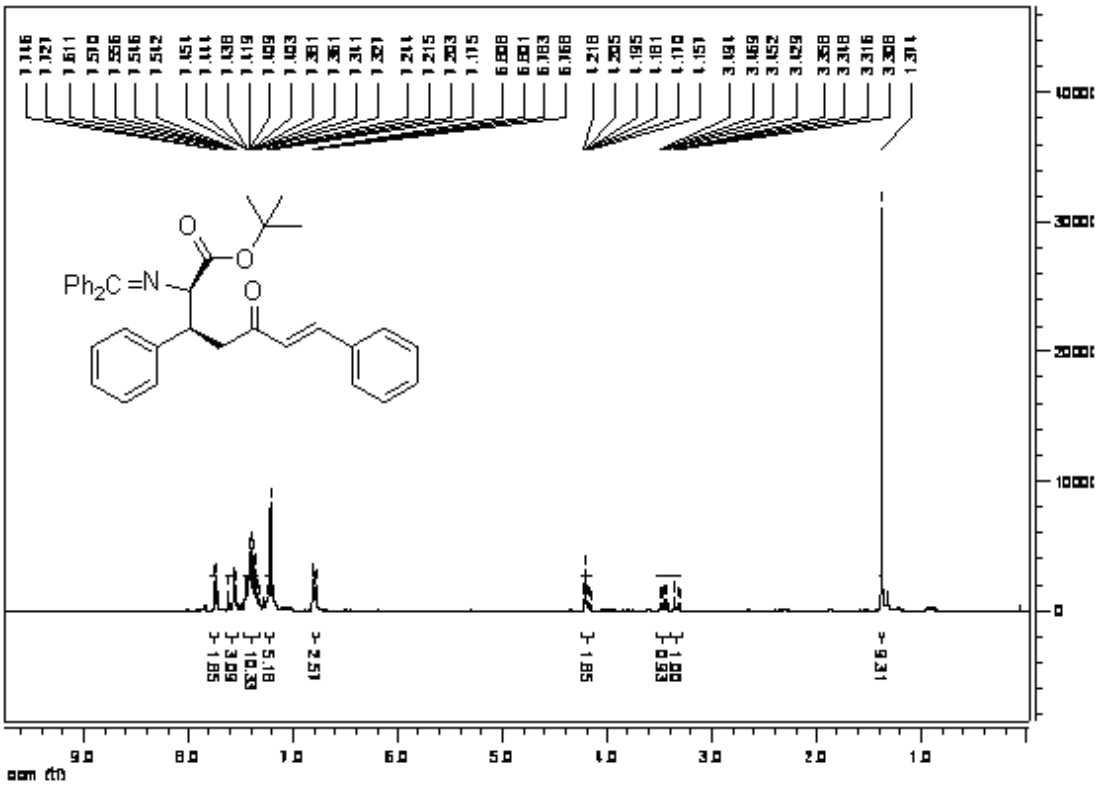

Ph2C =N
O
O
O
198.524
111.358
110.296
143.168
141.625
139.633
136.513
131.945
130.579
129.405
129.102
128.829
128.591
128.513
128.452
128.354
128.276
127.162
126.768
81.515
11.230
45.081
40.109
28.128
21.898
ppm (f1)

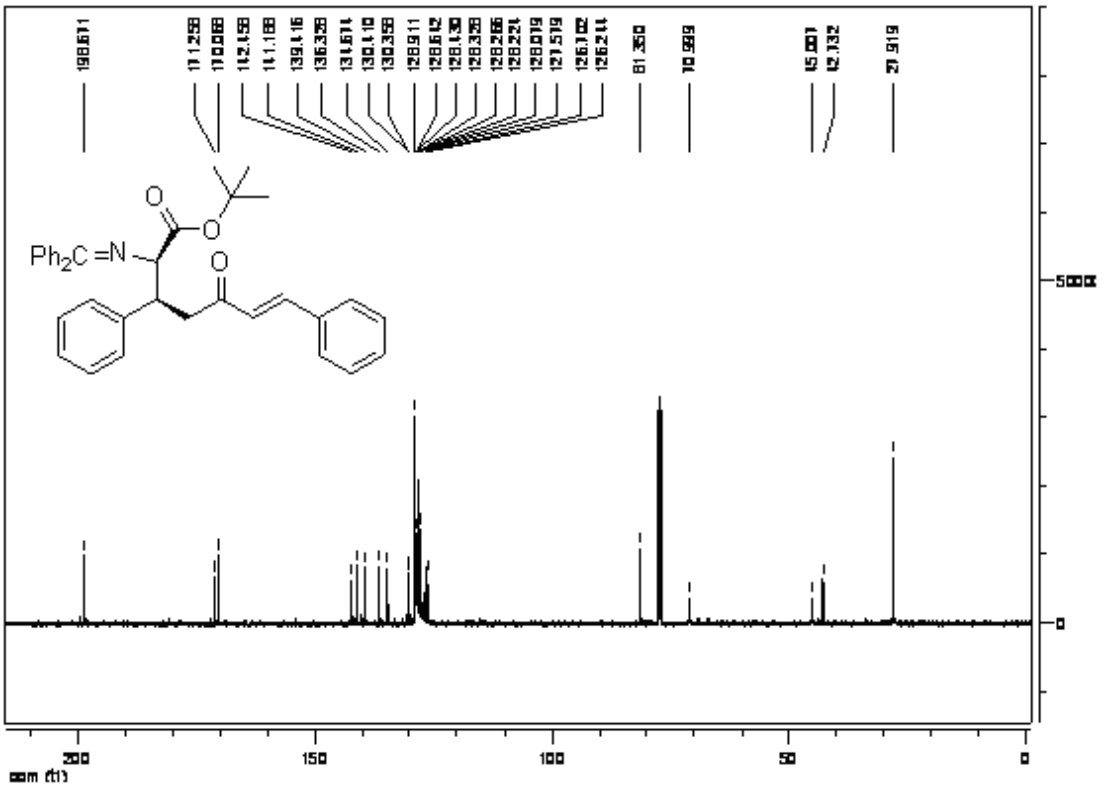

Ph2C =N
O
O
O
O

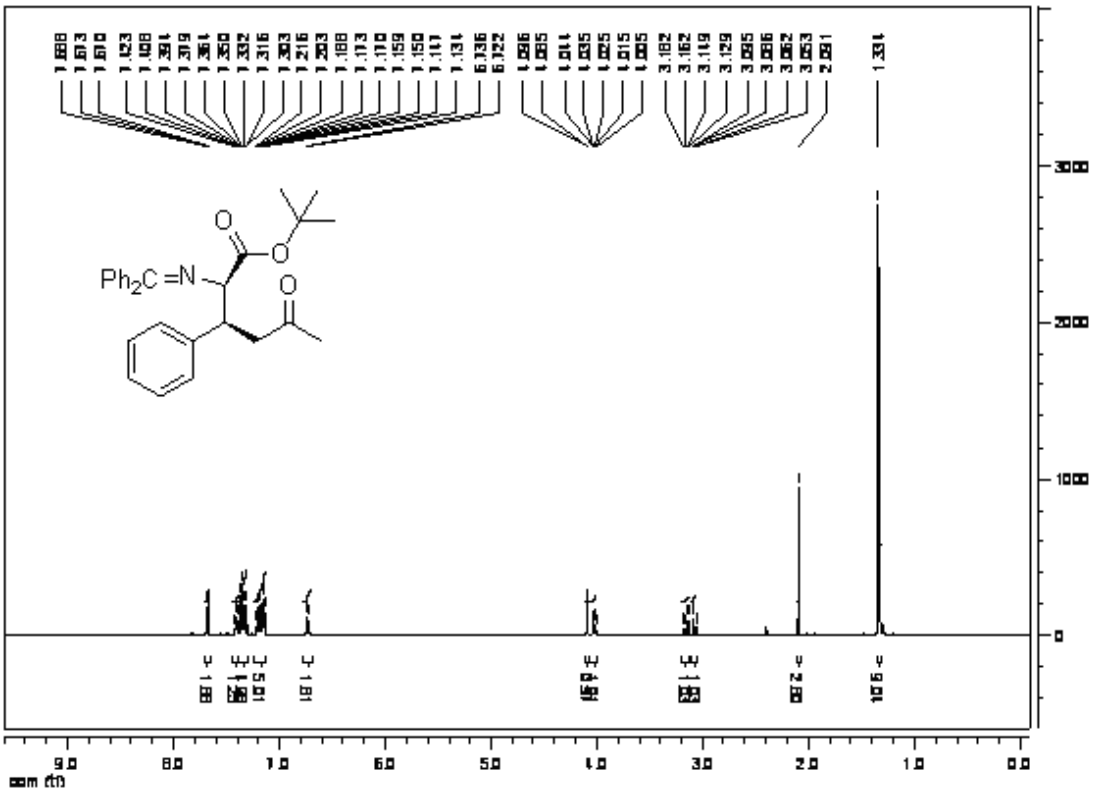

Ph2C =N
O
O
O
O

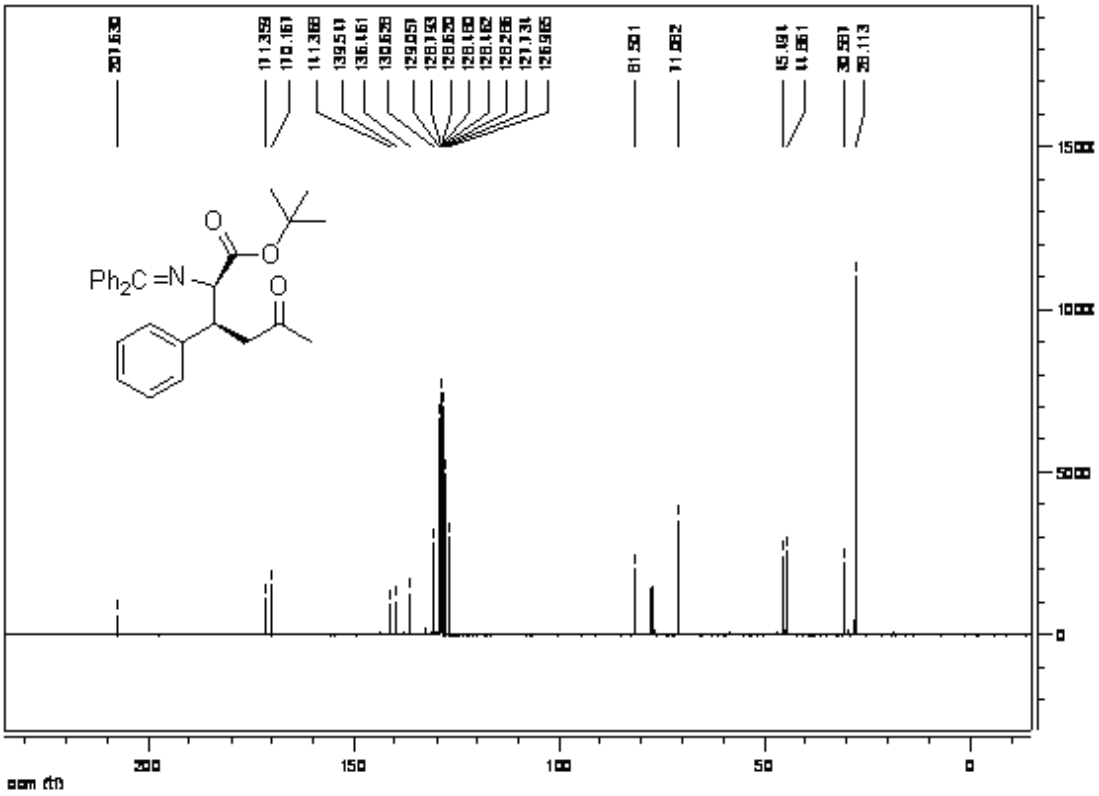

Ph2C =N
O
O
O
O
O
1.343
4.00
3.00
2.00
1.00
0.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

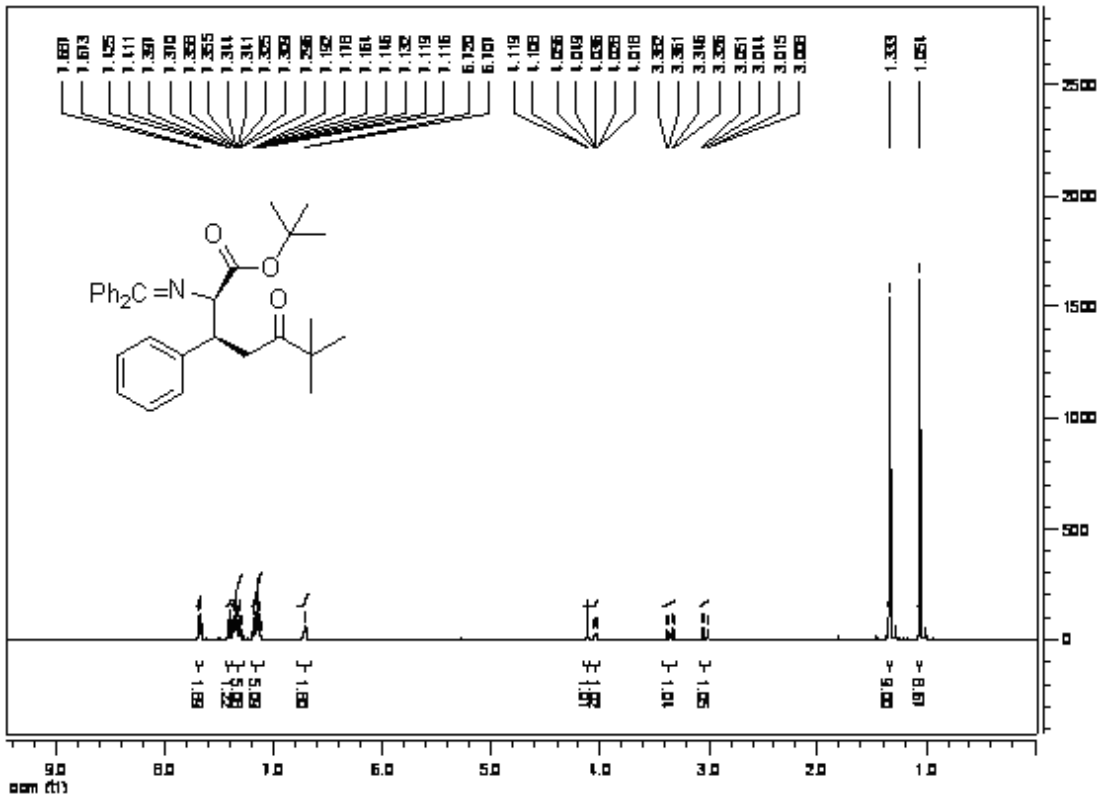

Ph2C =N
O
O
O
O
O
15000
10000
5000
0
200
150
100
50
0
ppm (t1)

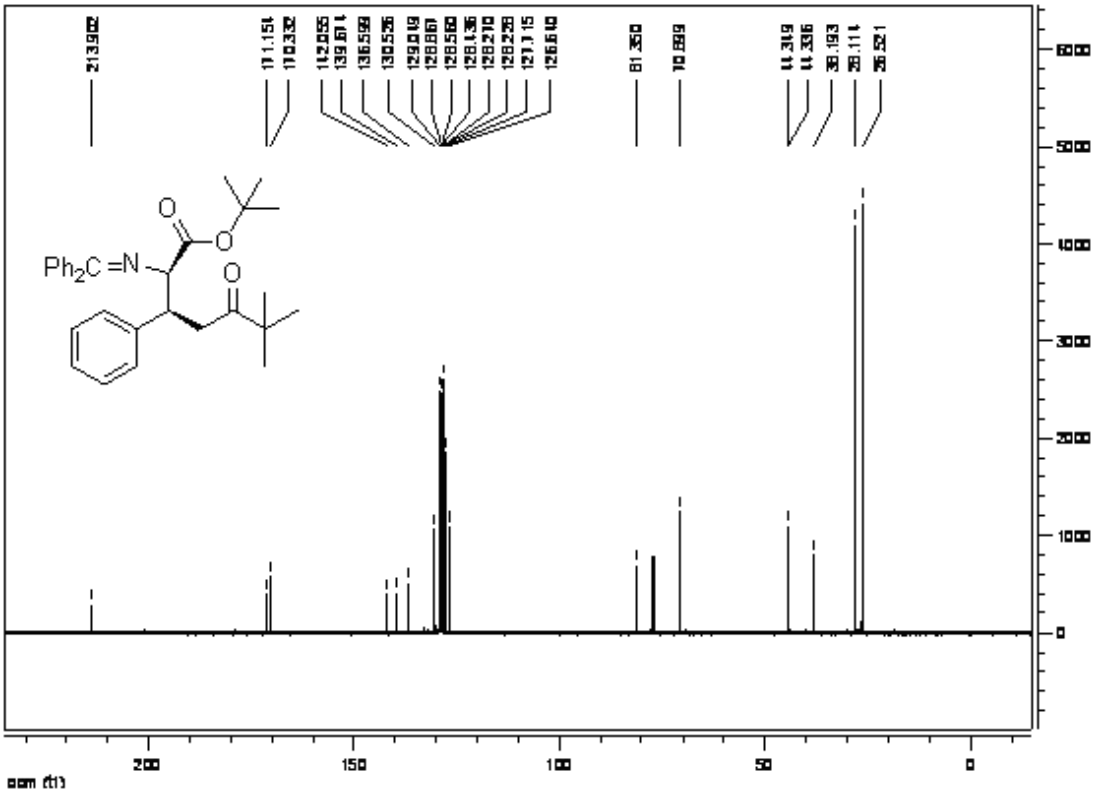


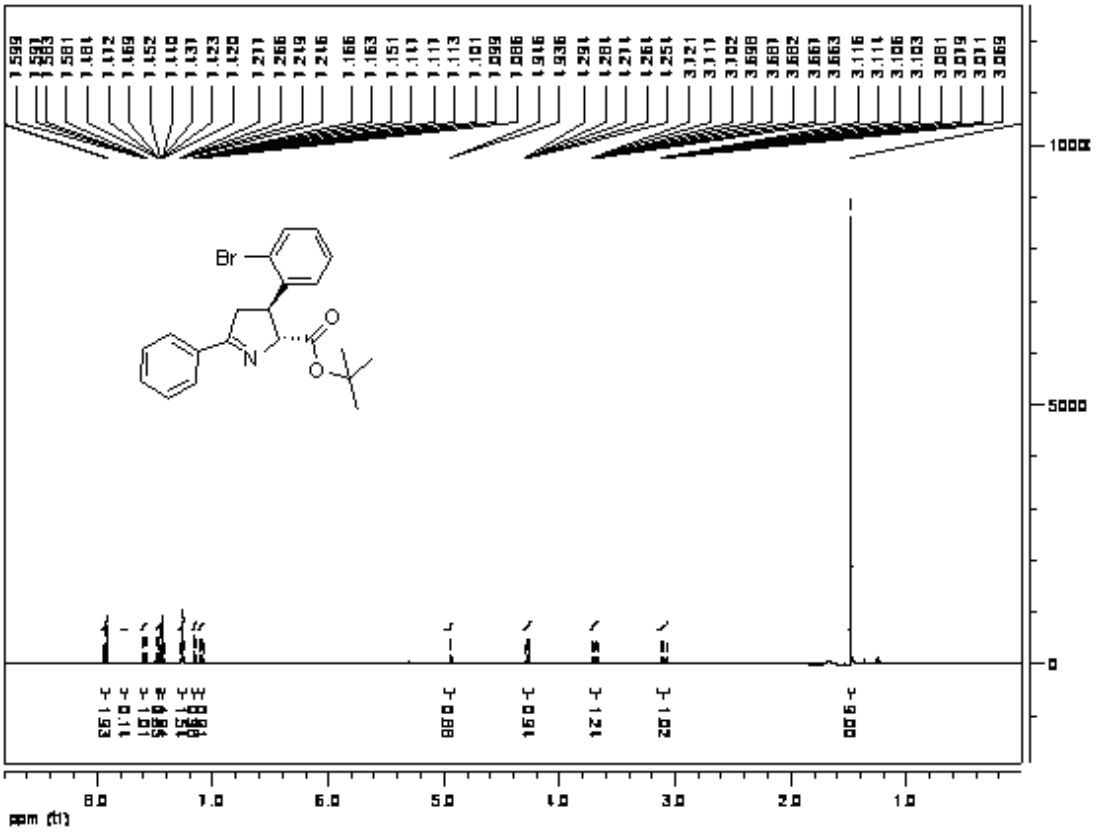


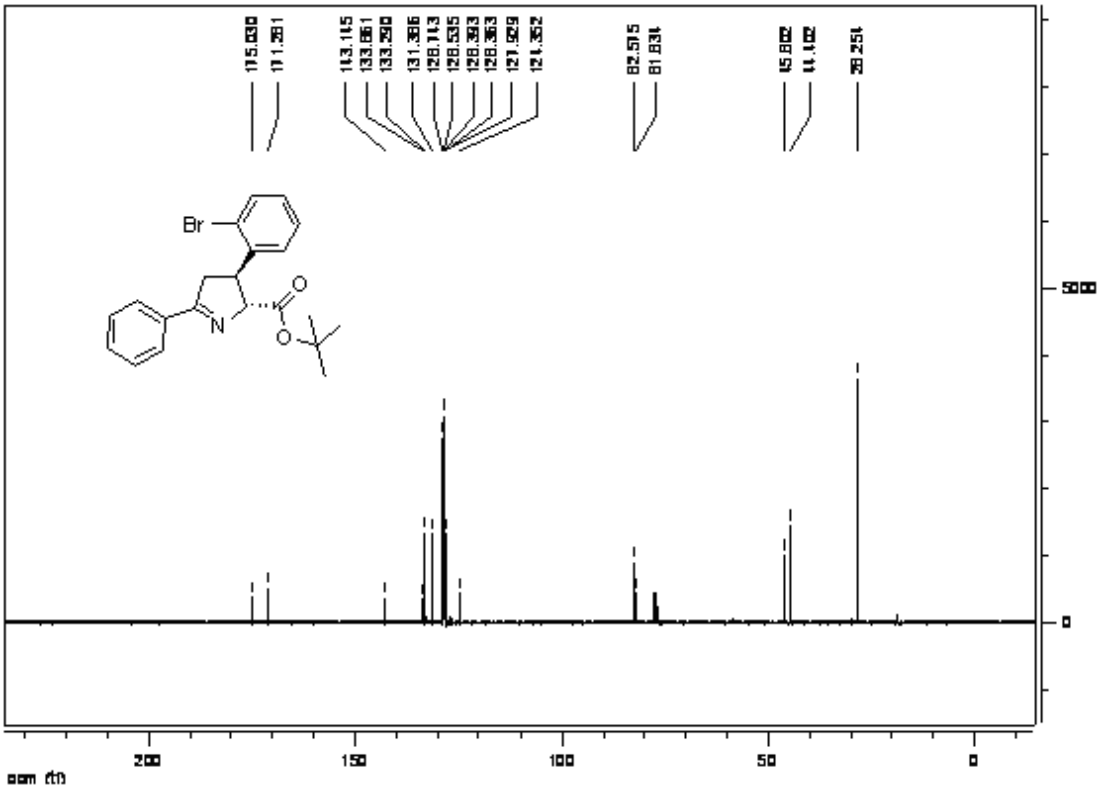

Ph2C =N
O
O
O
ppm (f1)

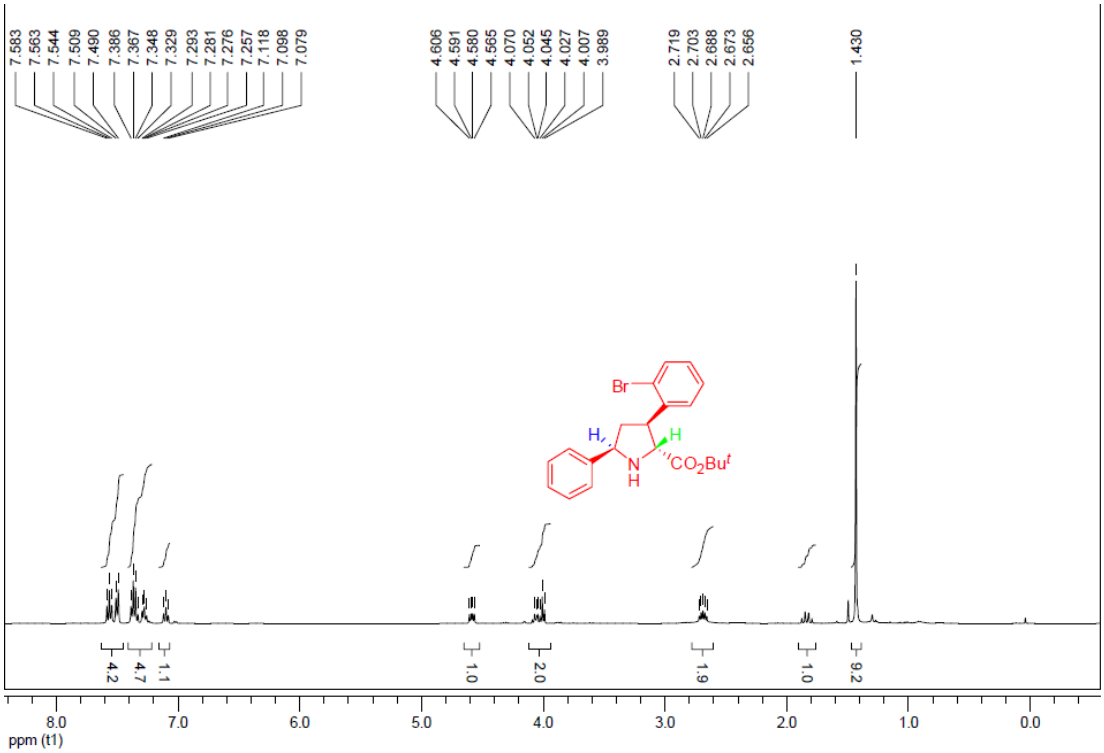

Ph2C =N
O
O
O
ppm (f1)

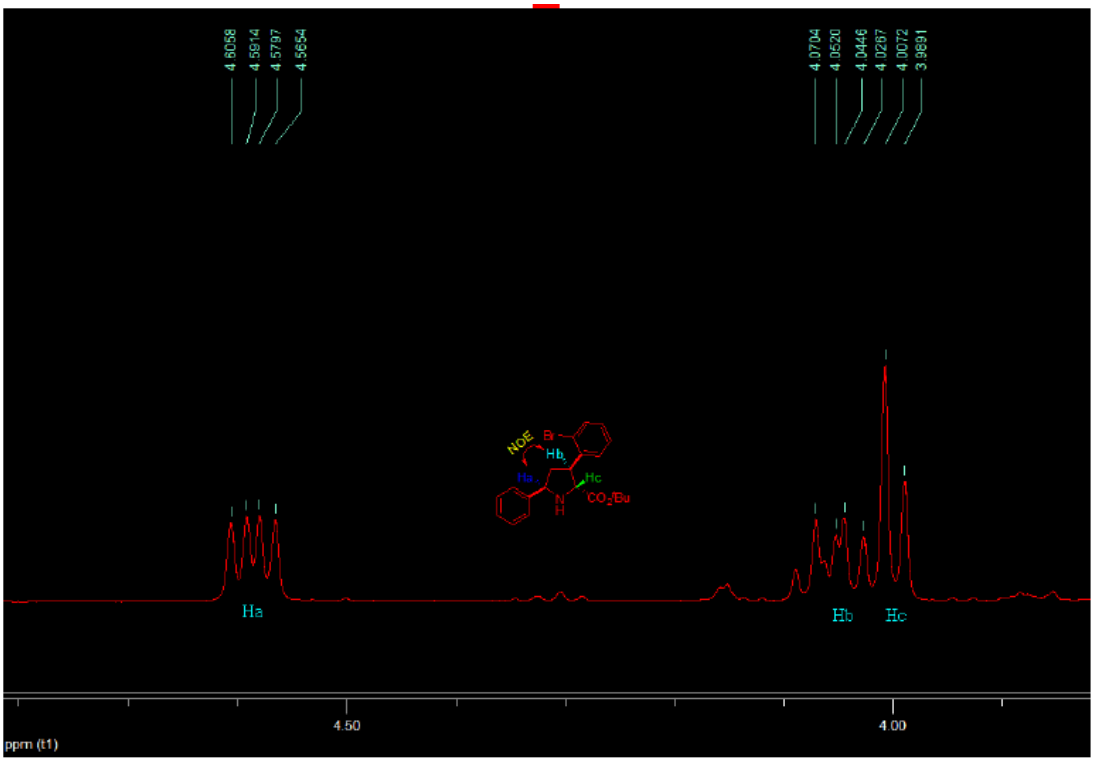

Ph2C =N
O
O
O
ppm (t1)

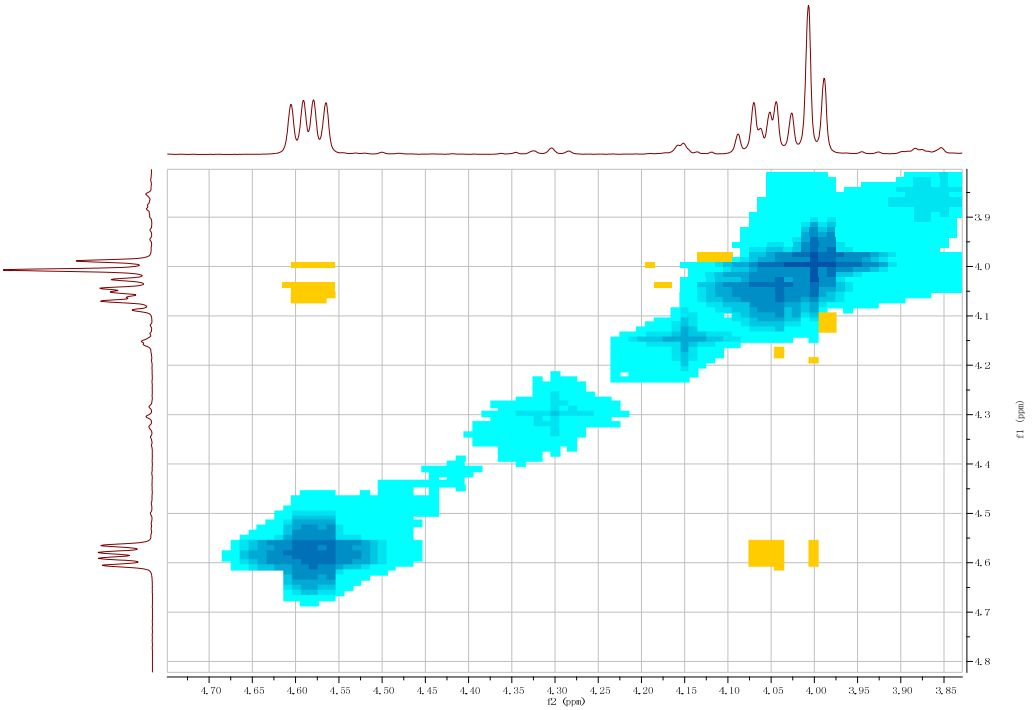

Ph2C =N
O
O
O
ppm (t1)

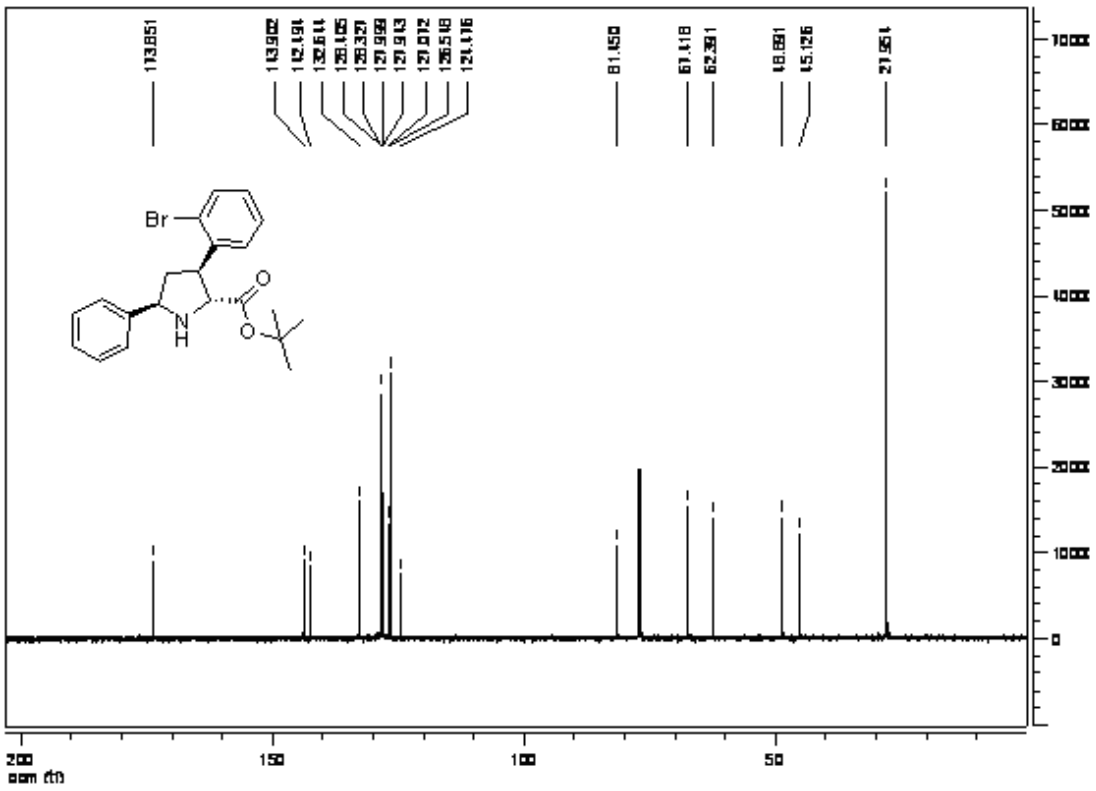

Br
N
O
O
ppm (t1)

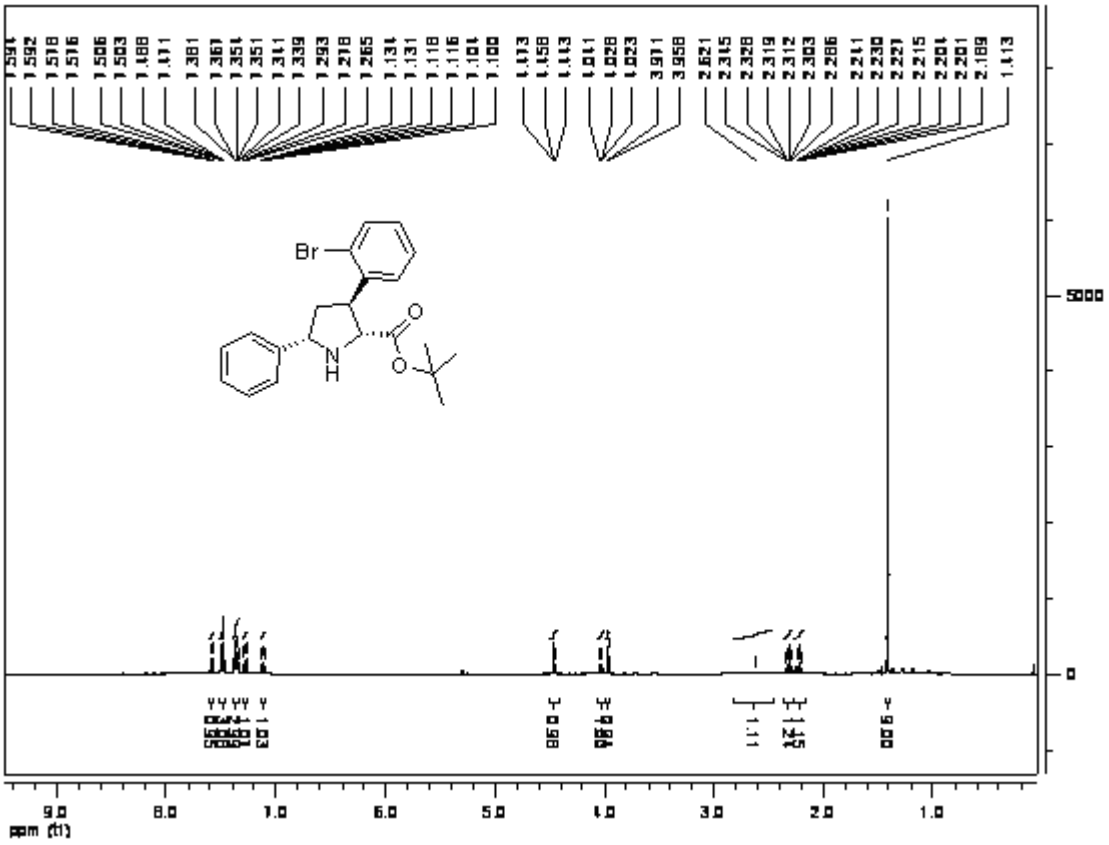

Br
N
O
O
ppm (t1)

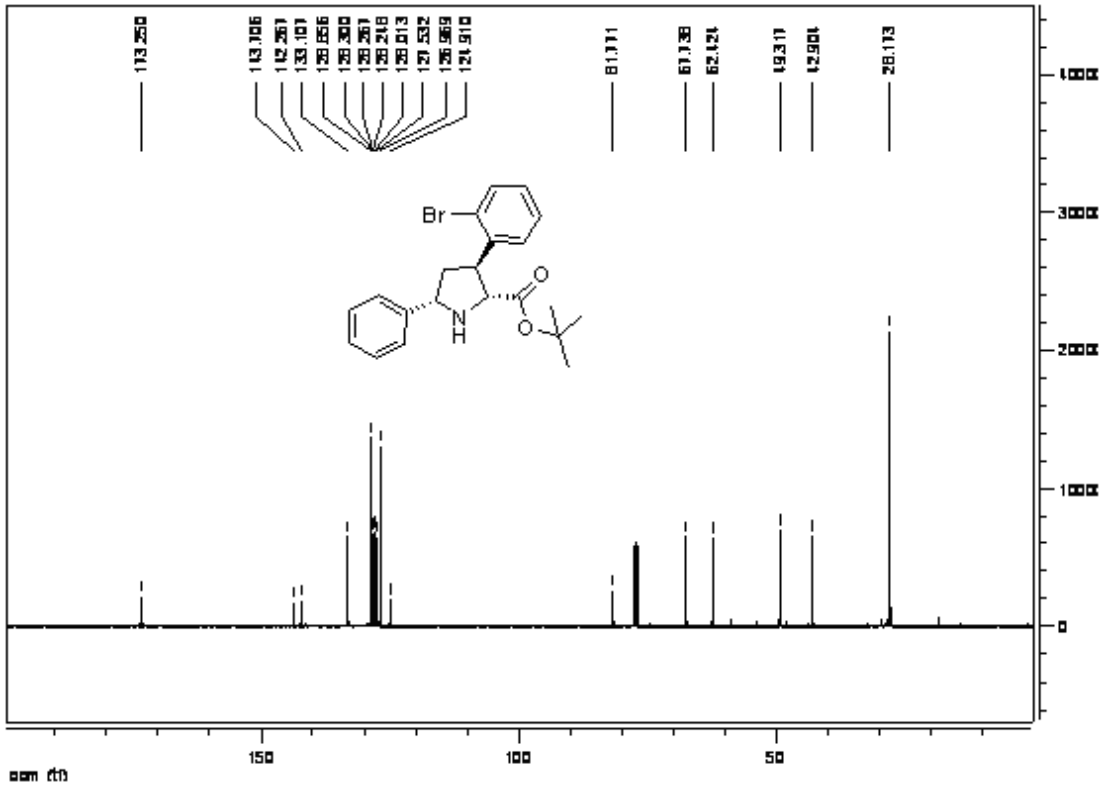

7.583
7.563
7.544
7.509
7.490
7.386
7.367
7.348
7.329
7.293
7.281
7.276
7.257
7.118
7.098
7.079
4.606
4.591
4.580
4.565
4.070
4.052
4.045
4.027
4.007
3.989
2.719
2.703
2.688
2.673
2.656
1.430
Br
H
H
N
H
CO2But
4.2
4.7
1.1
1.0
2.0
1.9
1.0
9.2
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

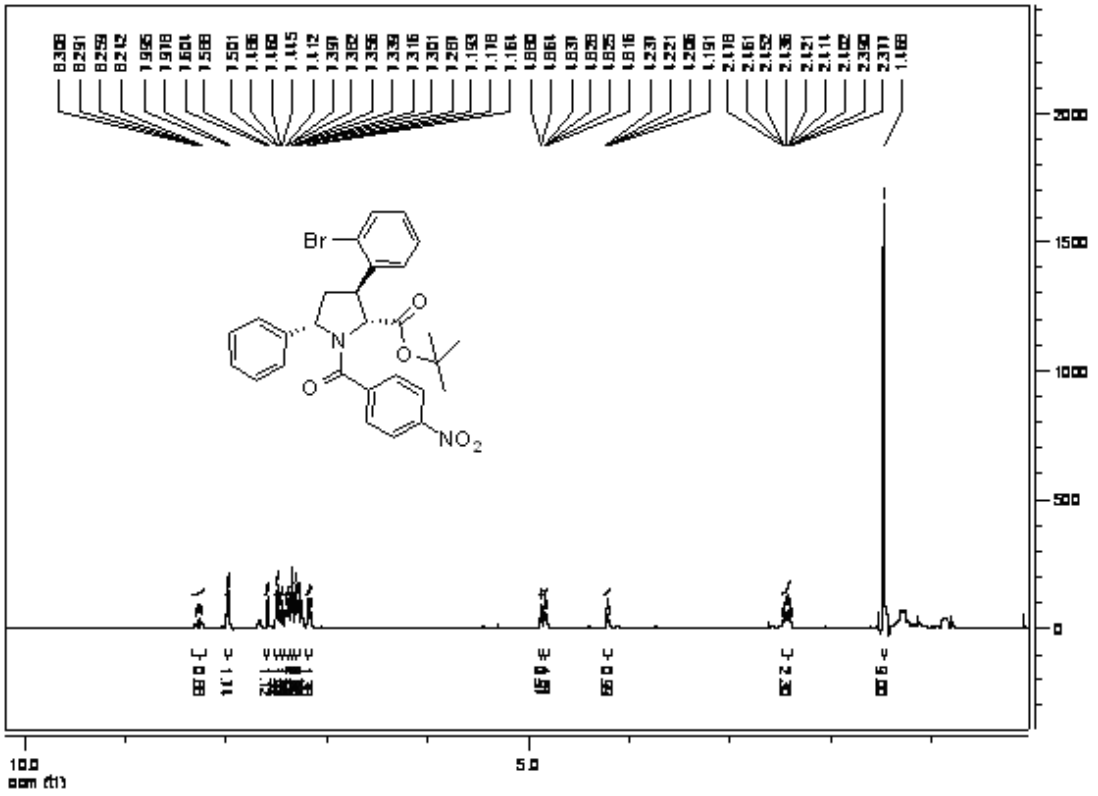

4.6058
4.5914
4.5797
4.5654
4.0704
4.0520
4.0446
4.0267
4.0072
3.9691
NOE
Br
Hb
Ha
Hc
N
H
CO2tBu
Ha
Hb
Hc
4.50
4.00
ppm (t1)

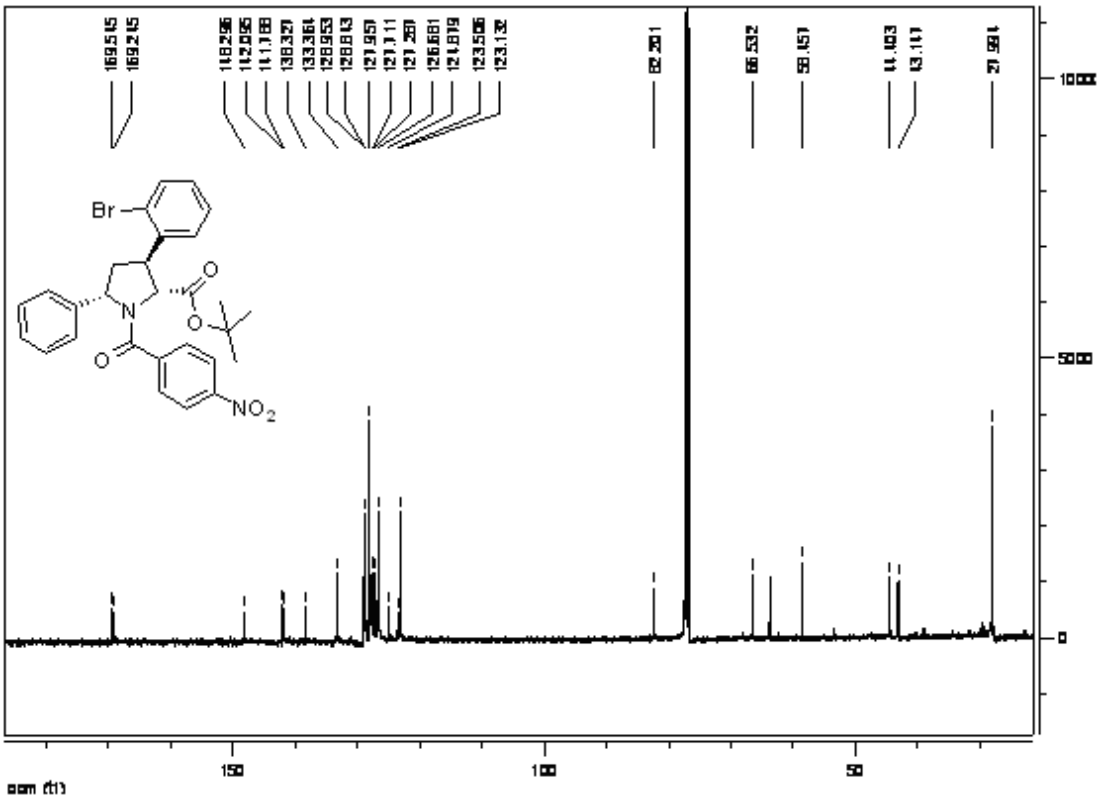

4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85
f2 (ppm)
3.9 4.0 4.1 4.2 4.3 4.4 4.5 4.6 4.7 4.8
f1 (ppm)

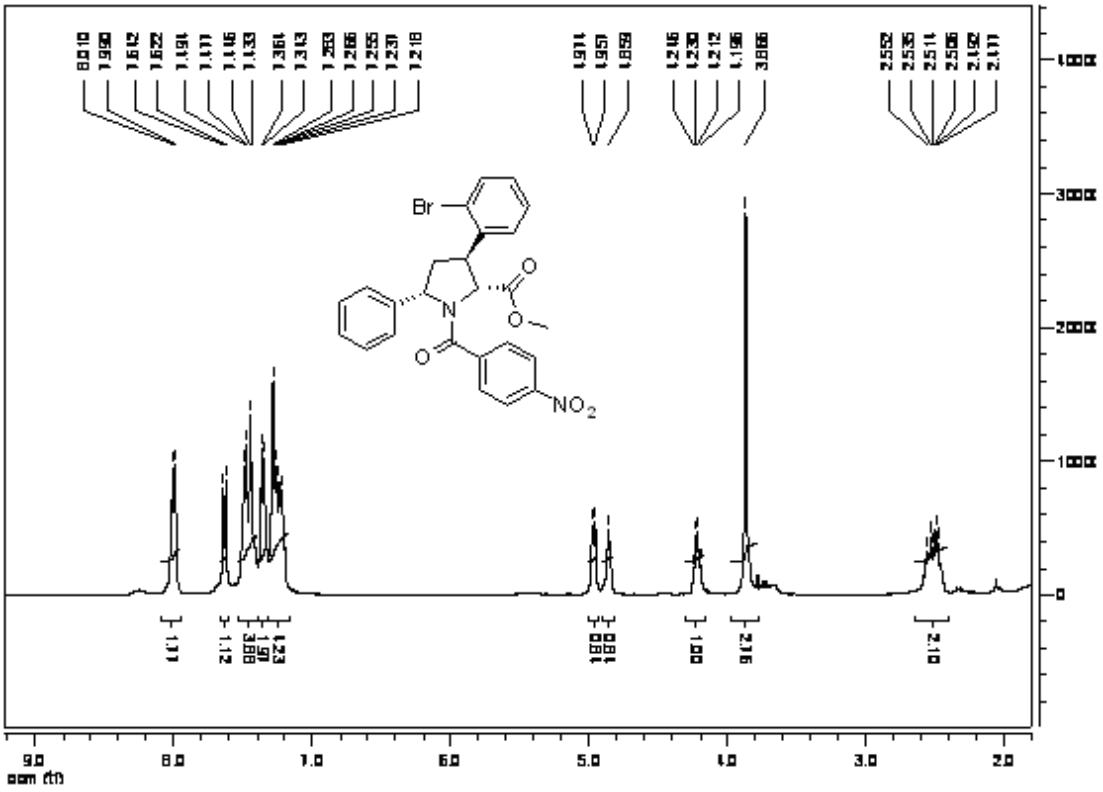

133.851
113.902
112.191
132.611
131.105
130.327
127.998
127.913
127.012
126.548
124.116
81.450
63.418
62.391
48.881
45.126
27.954
Br
O
O
N
H
200
150
100
50
ppm (f1)

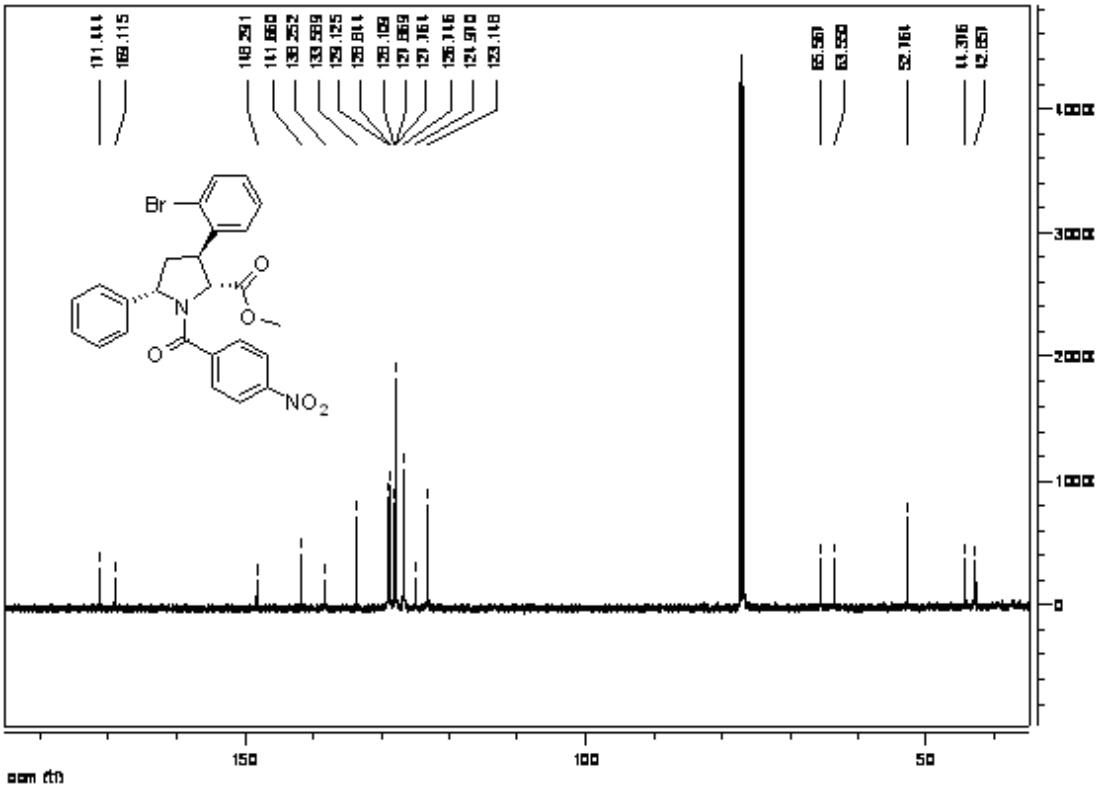

Br
O
N
H
O
5000
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (t1)

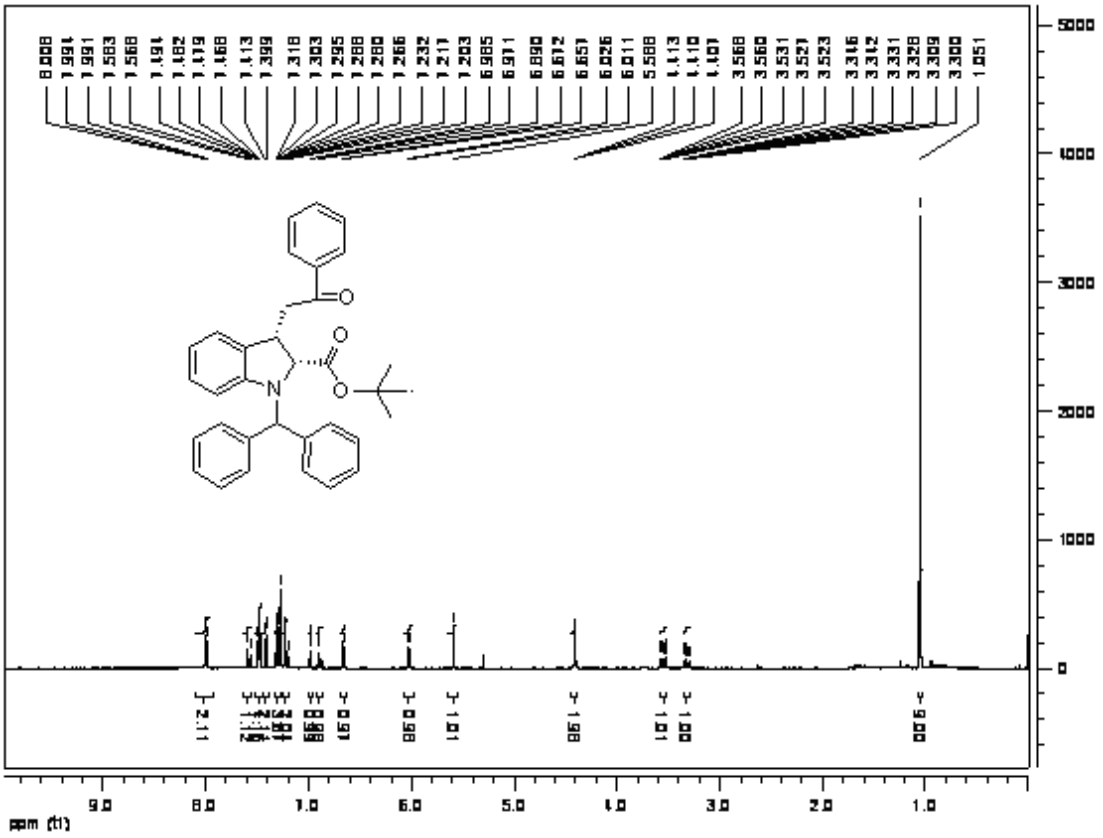

113.250
113.706
112.261
133.101
135.856
135.300
135.261
135.216
135.013
127.532
126.969
124.910
81.111
61.738
62.424
49.311
42.901
28.113
Br
O
N
H
O
4000
3000
2000
1000
0
150
100
50
ppm (t1)

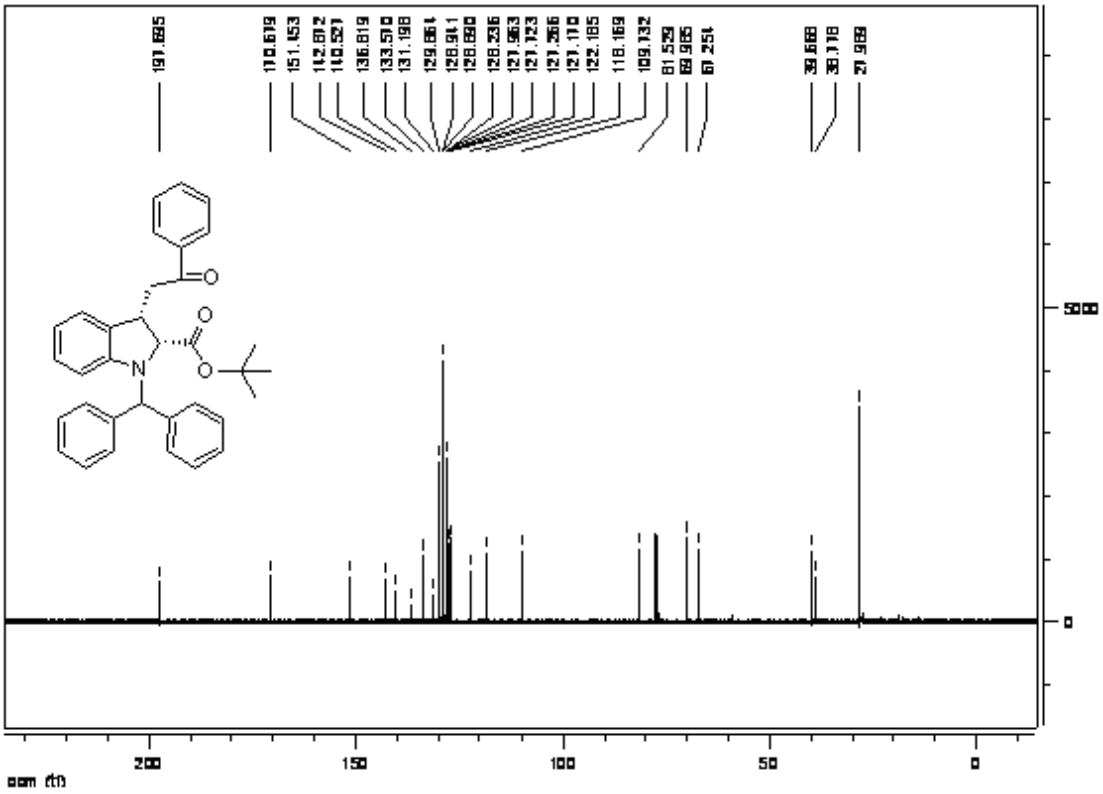

Br
O
N
O
O
O
NO2

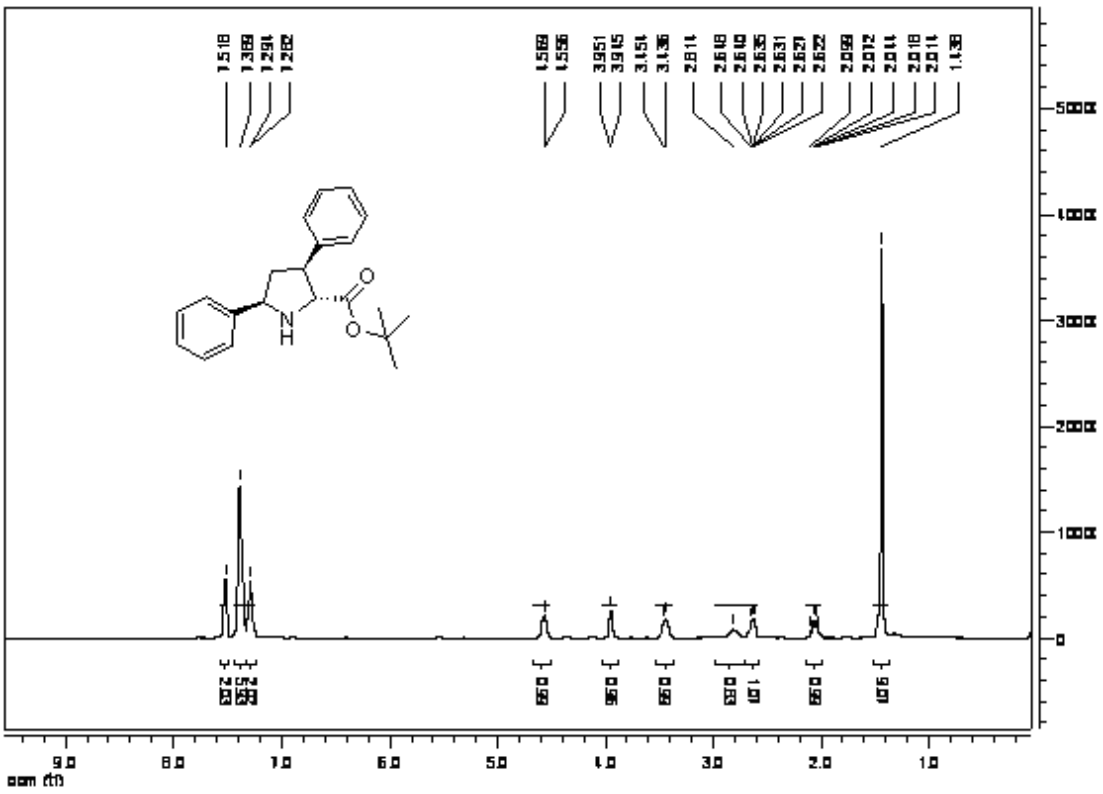

Br
O
N
O
O
O
NO2

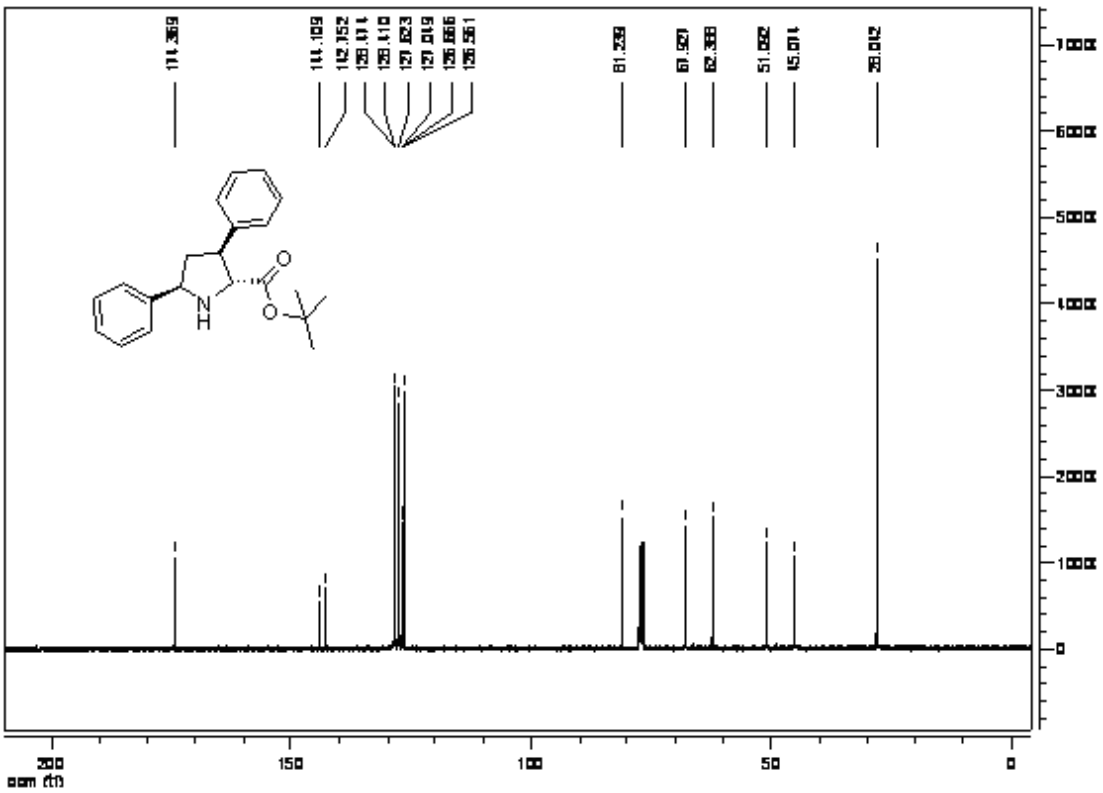

Br
N
O
O
O
NO2

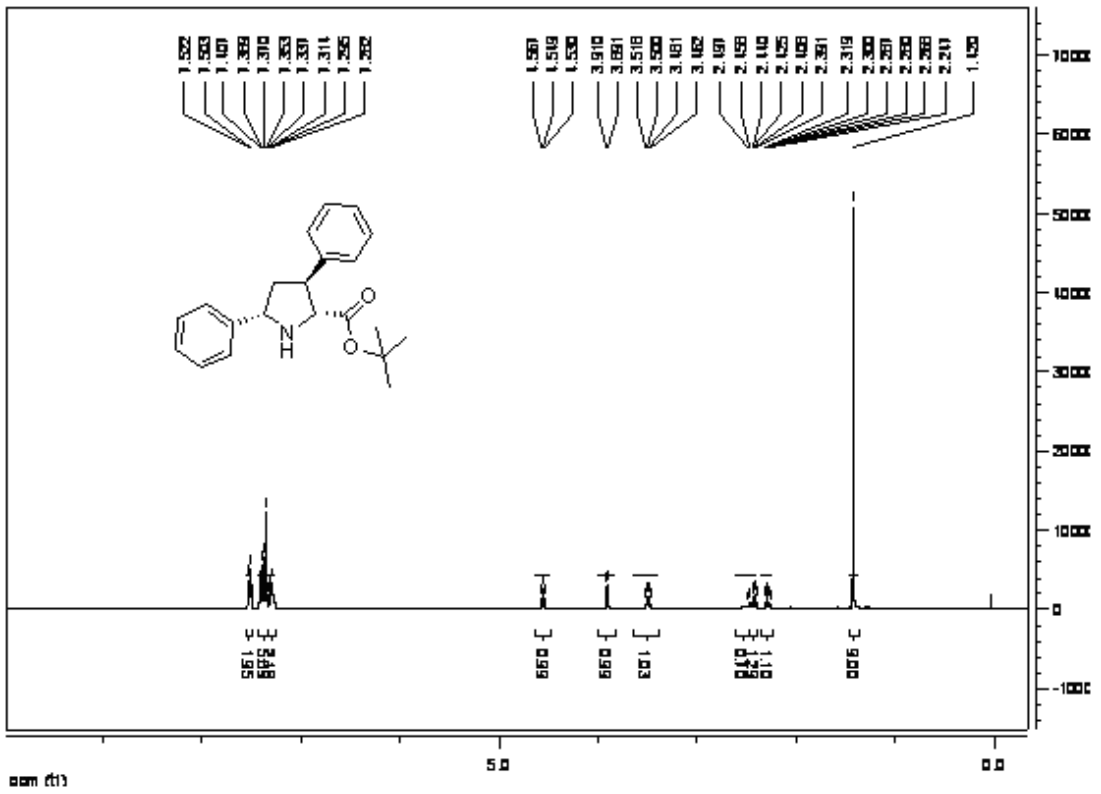

Br
N
O
O
O
NO2

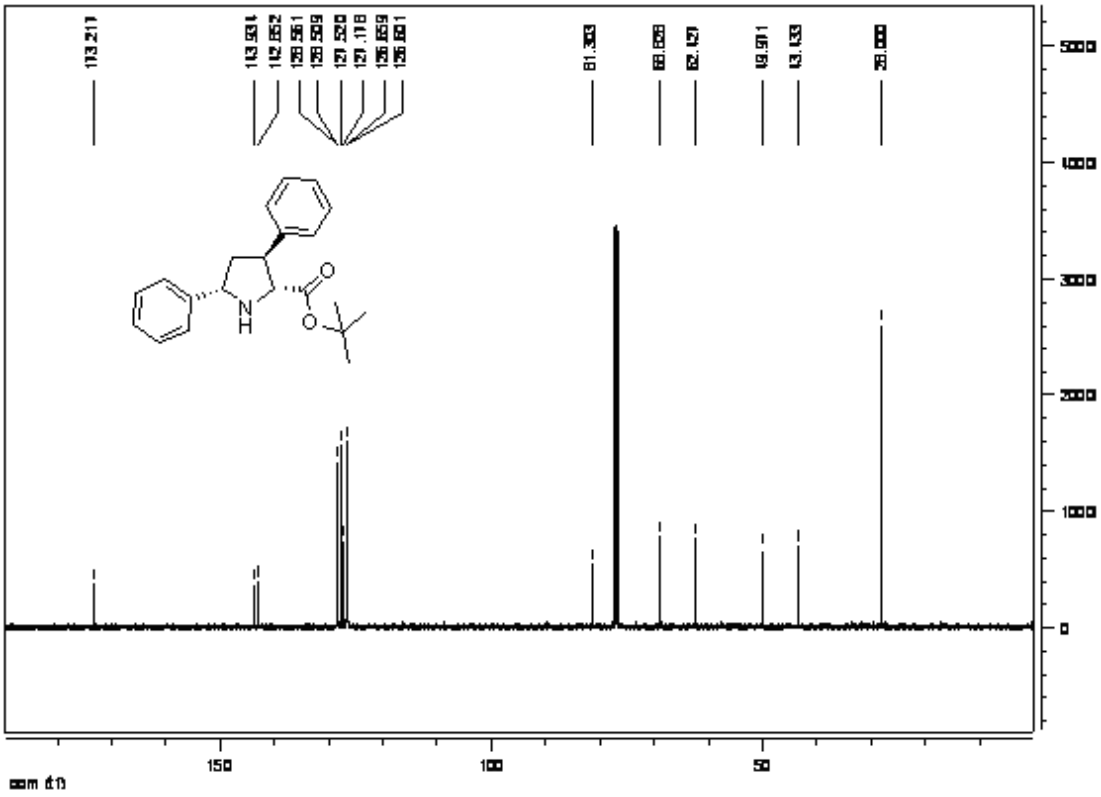


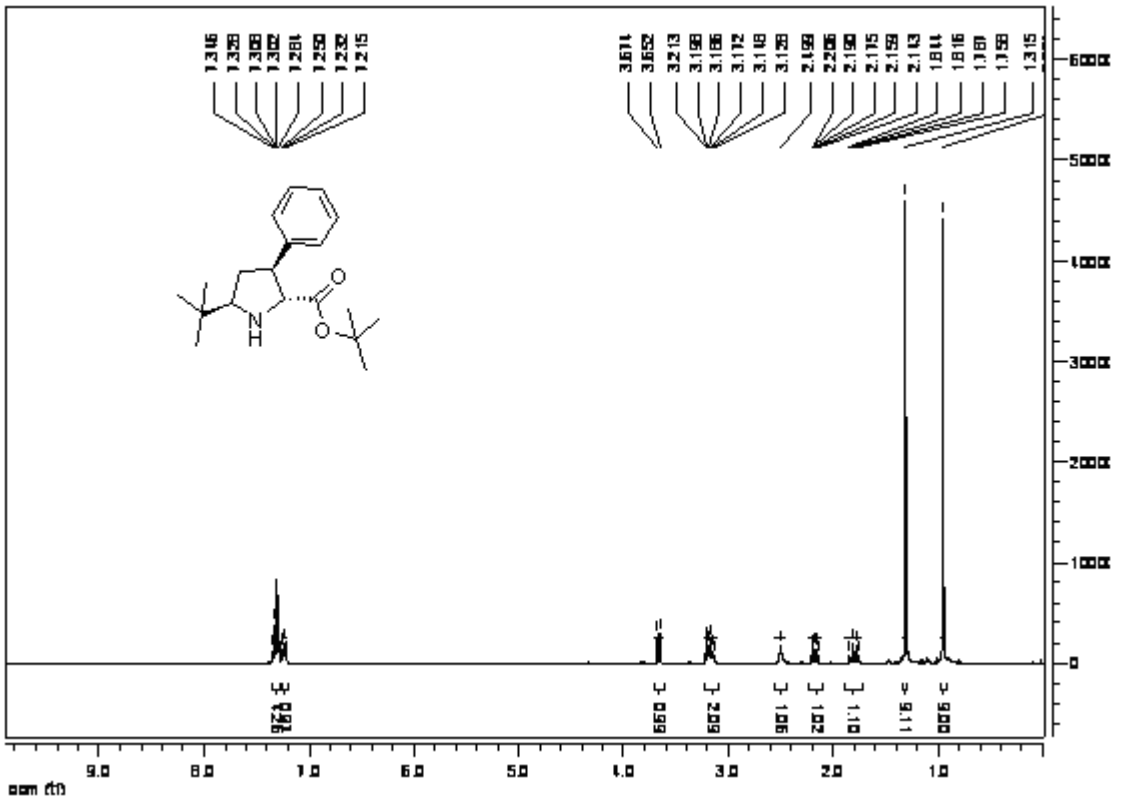


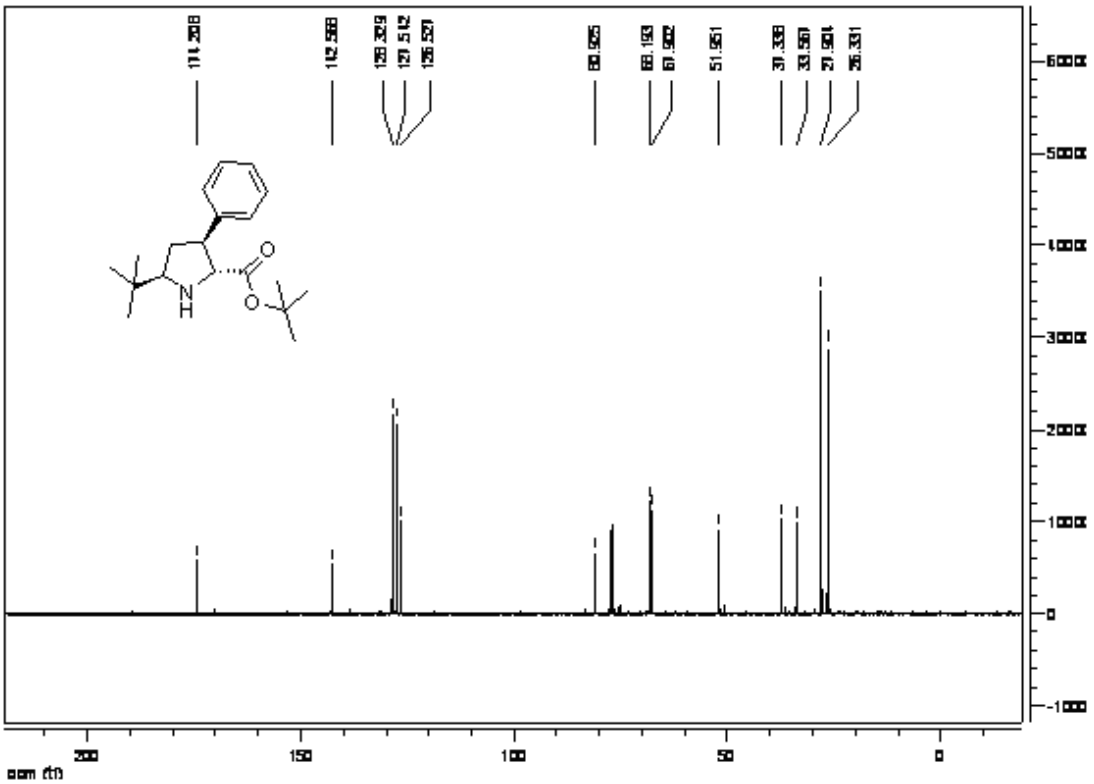


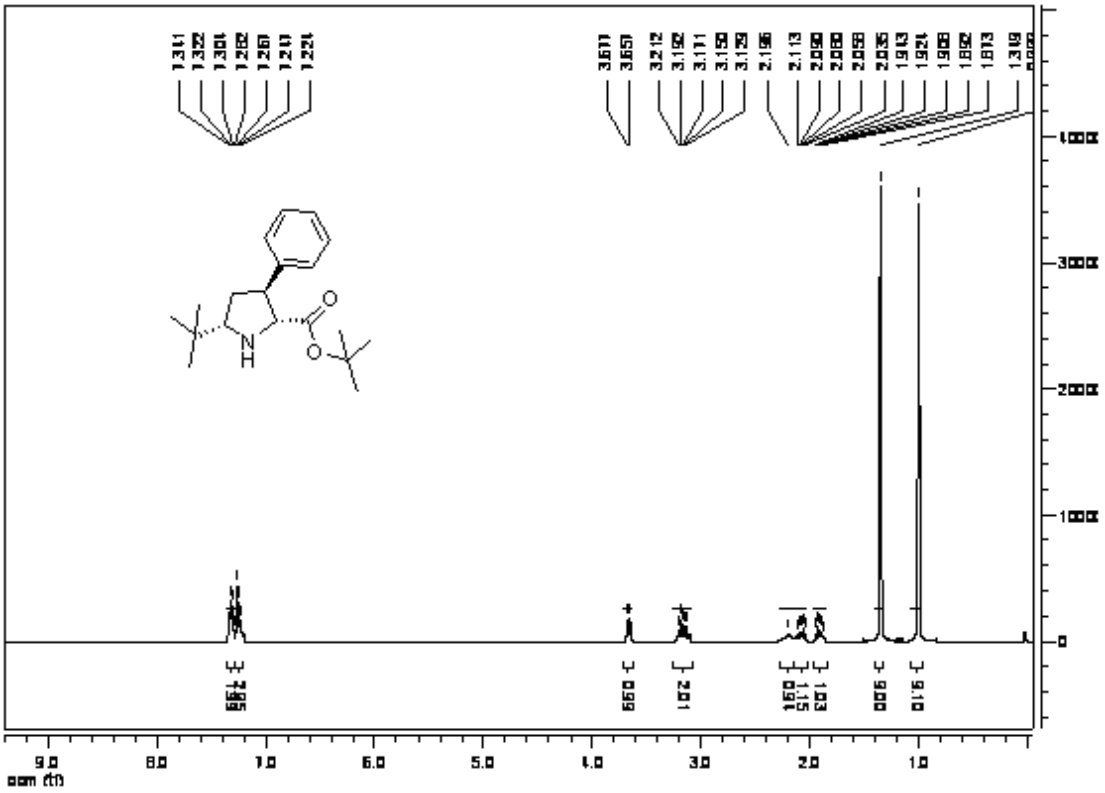


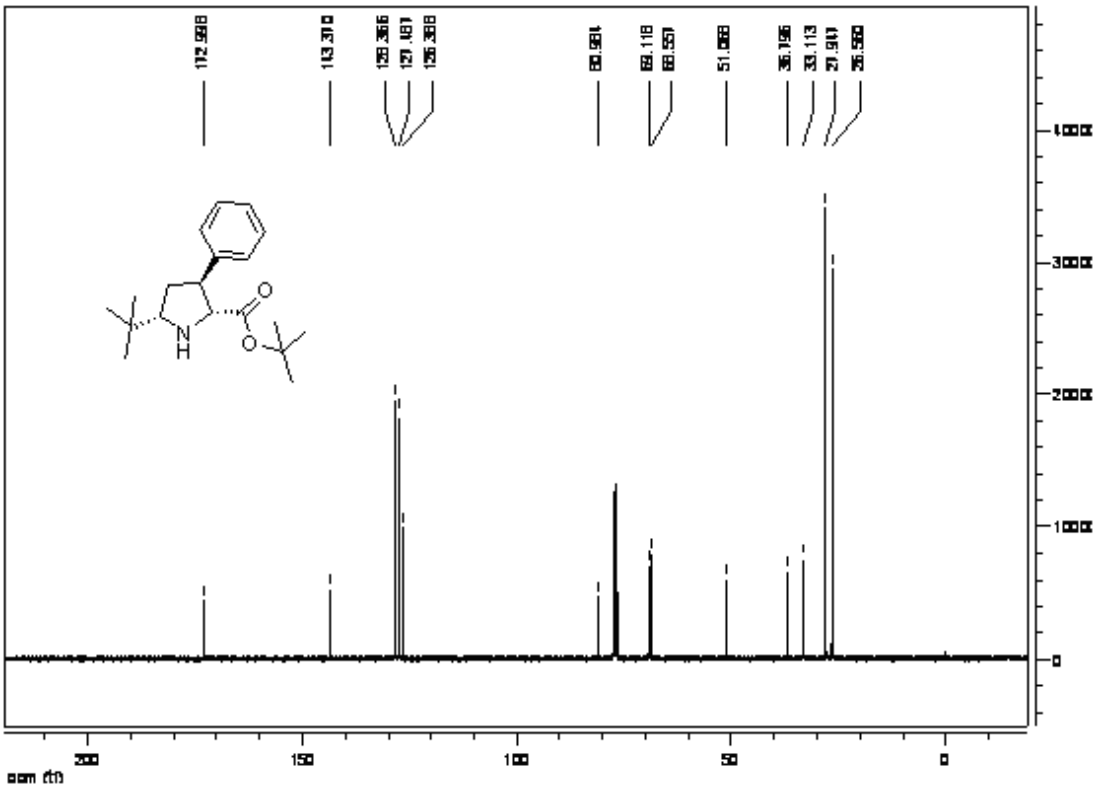


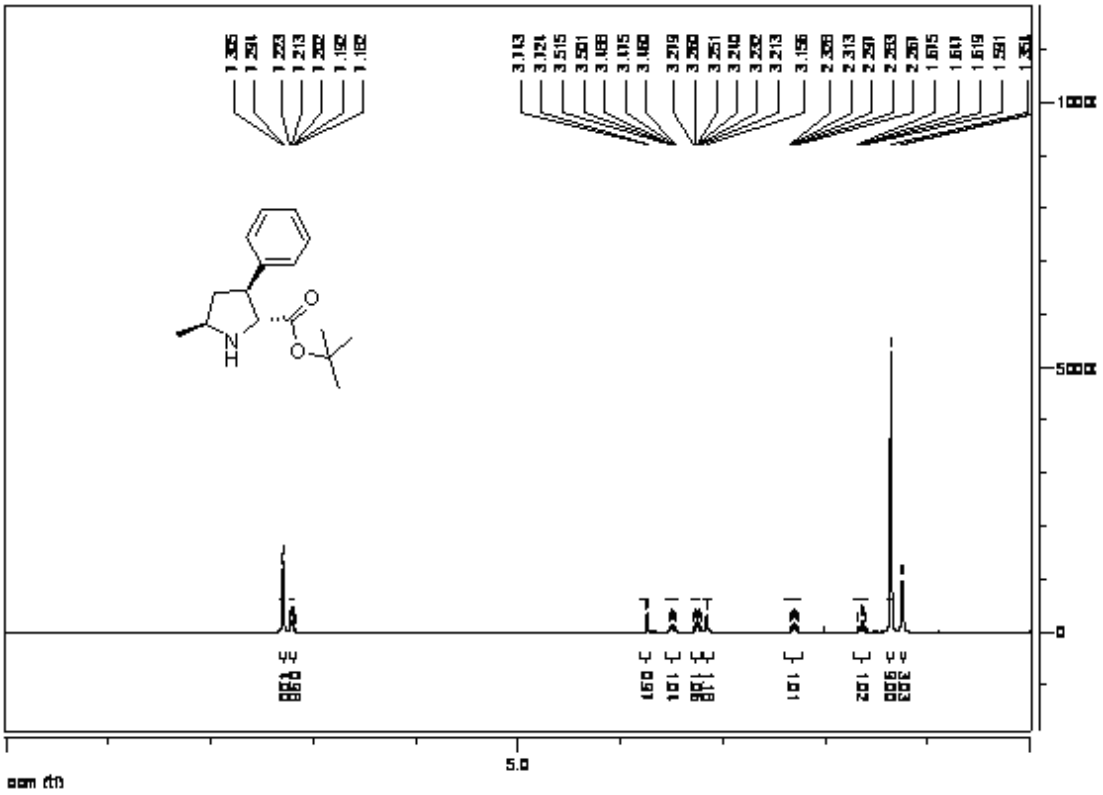


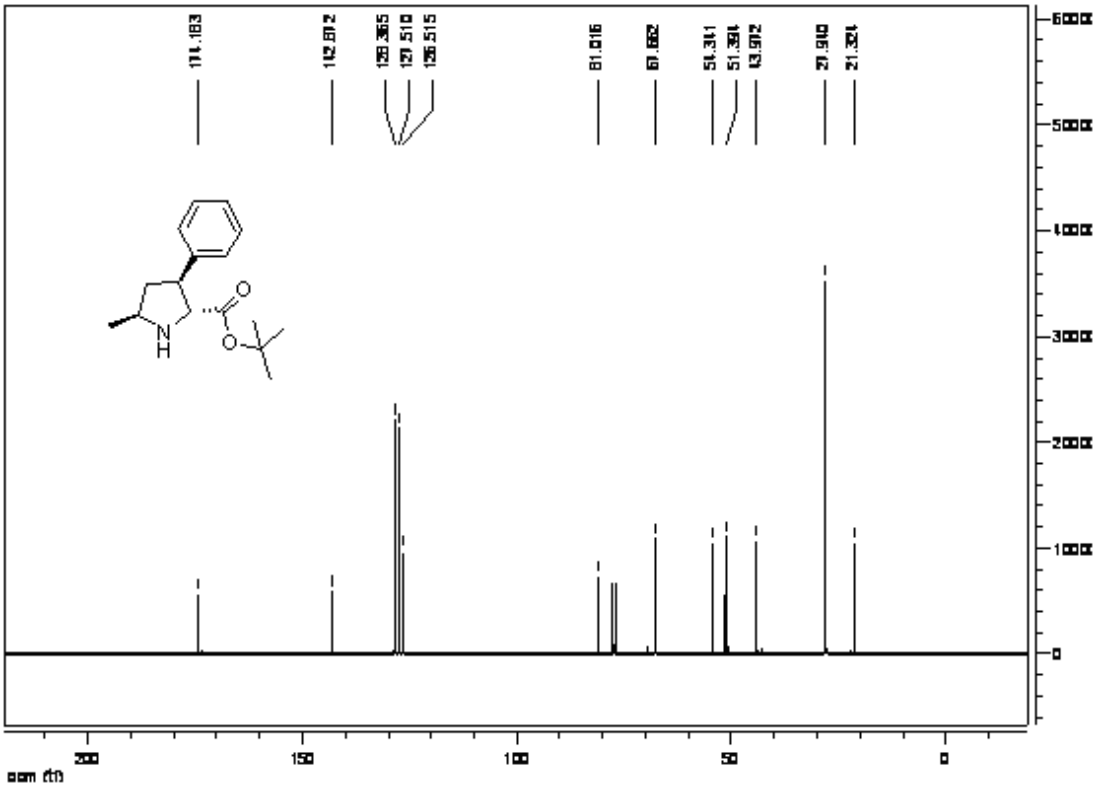


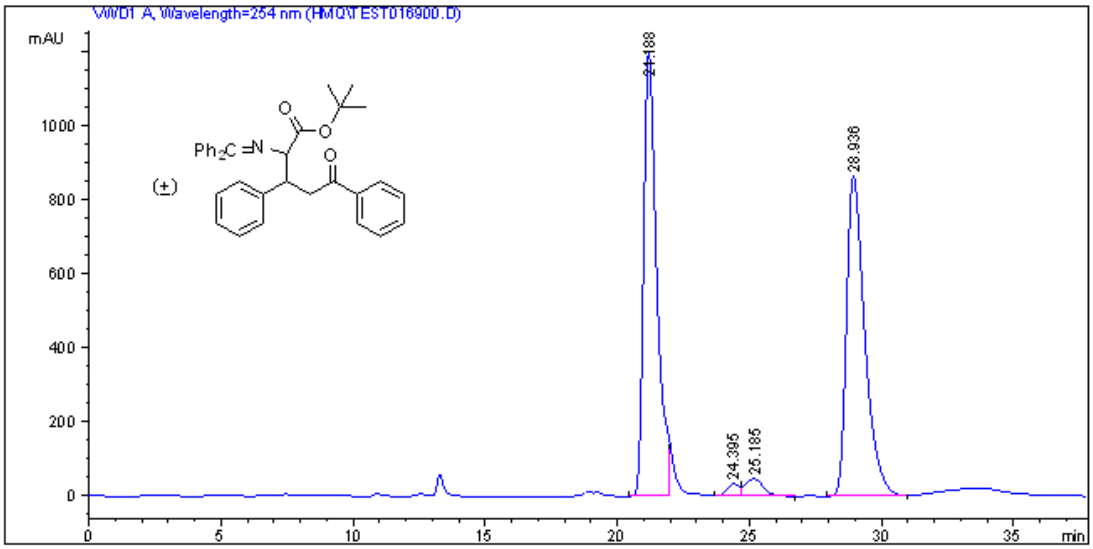






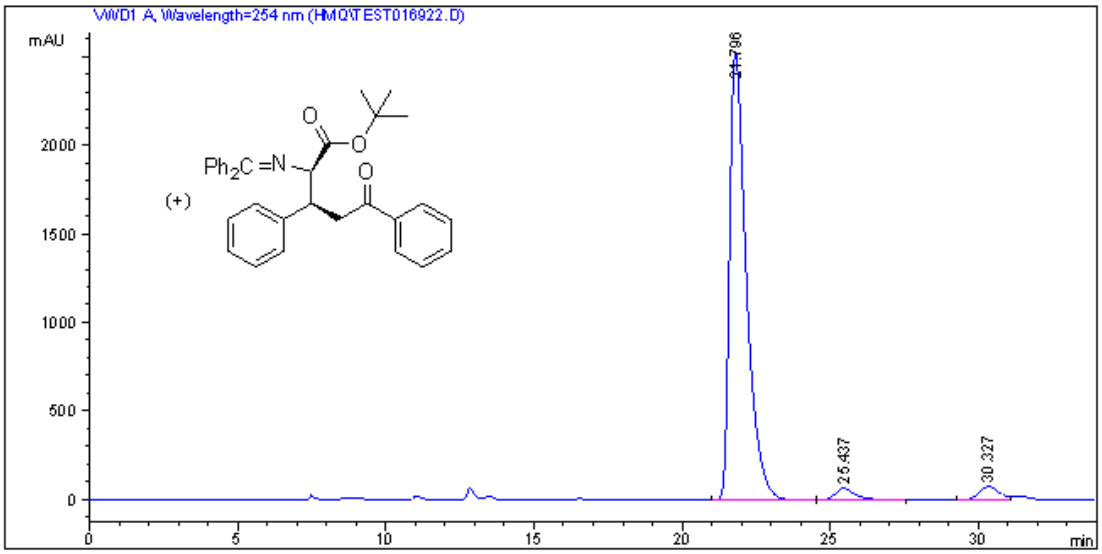






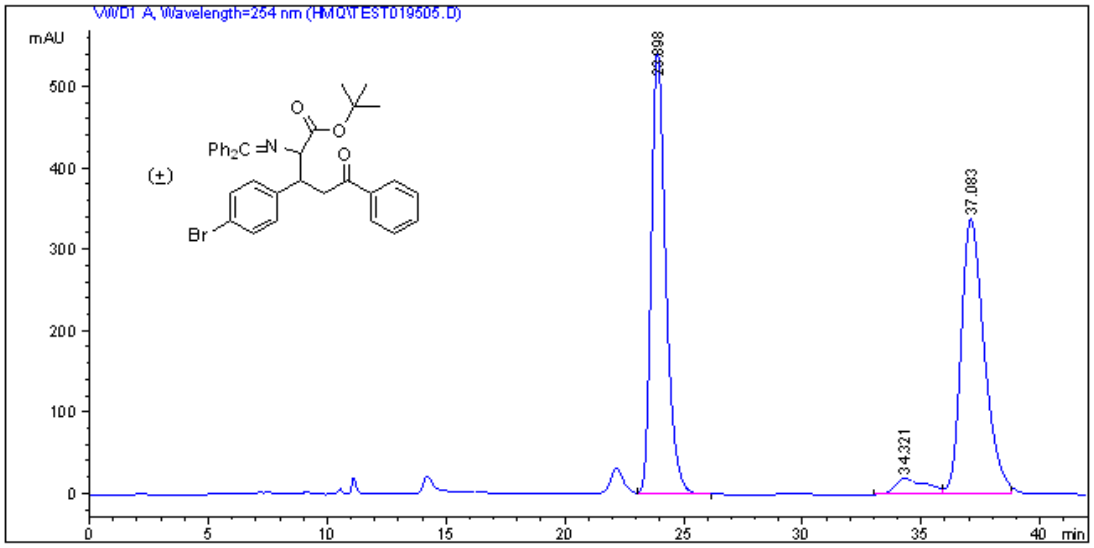
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.188	BBA	0.5196	4.13869e4	1197.79419	48.1231
2	24.395	VV	0.4825	1043.23901	32.98769	1.2130
3	25.185	VB	0.7334	2229.09375	46.31133	2.5919
4	28.936	VV	0.7218	4.13429e4	863.34637	48.0720



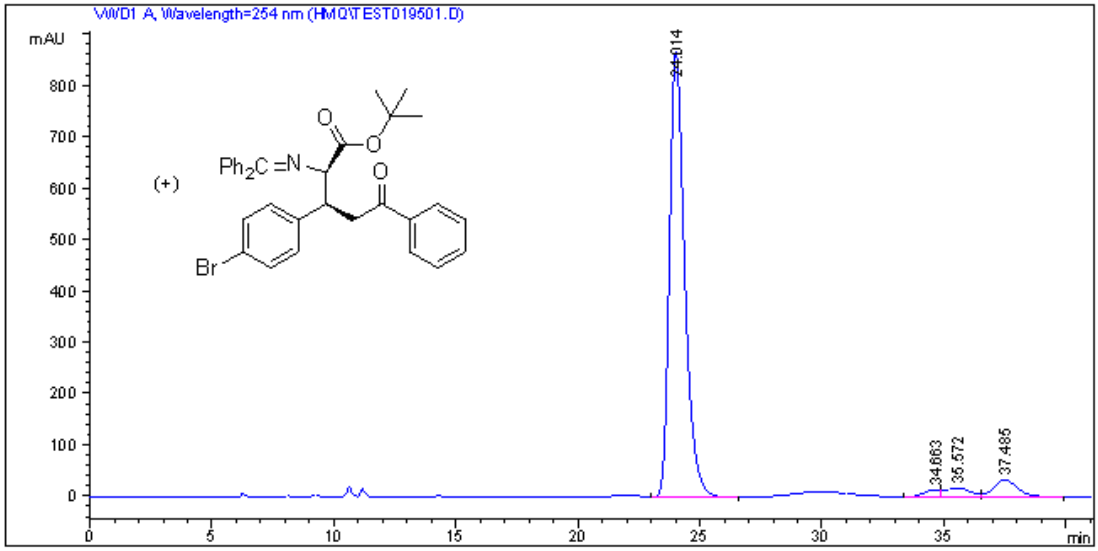
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.796	BV	0.5936	9.92737e4	2519.88696	93.7906
2	25.437	VB	0.6777	2973.49316	65.55968	2.8093
3	30.327	BV	0.7285	3598.88306	75.42698	3.4001
Totals :				1.05846e5	2660.87363	



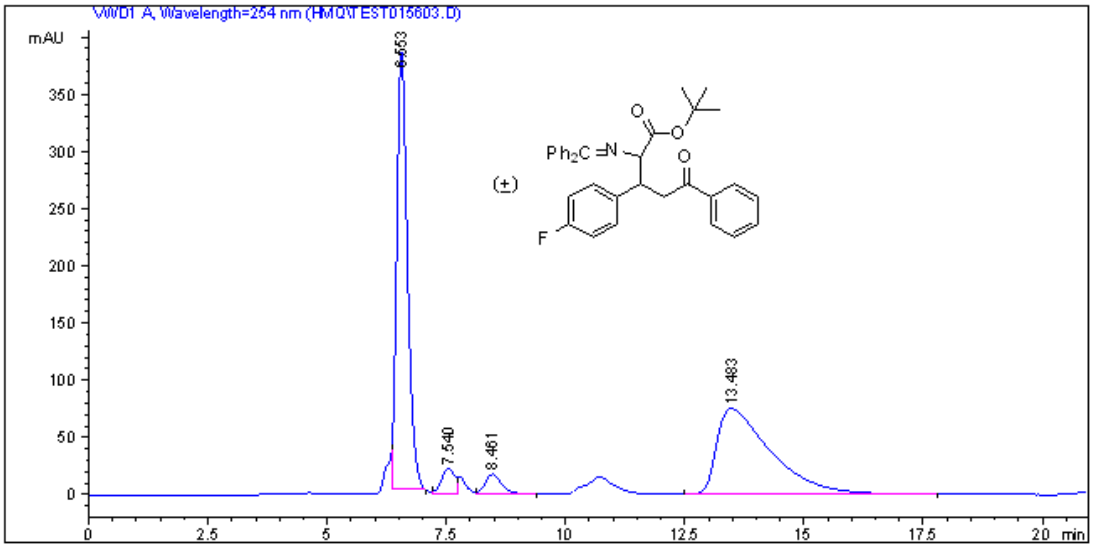
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.898	BB	0.6467	2.30223e4	542.28558	48.0725
2	34.321	BV	1.2760	1815.20227	19.69900	3.7903
3	37.083	VBA	1.0398	2.30533e4	338.23761	48.1372
Totals :				4.78908e4	900.22219	



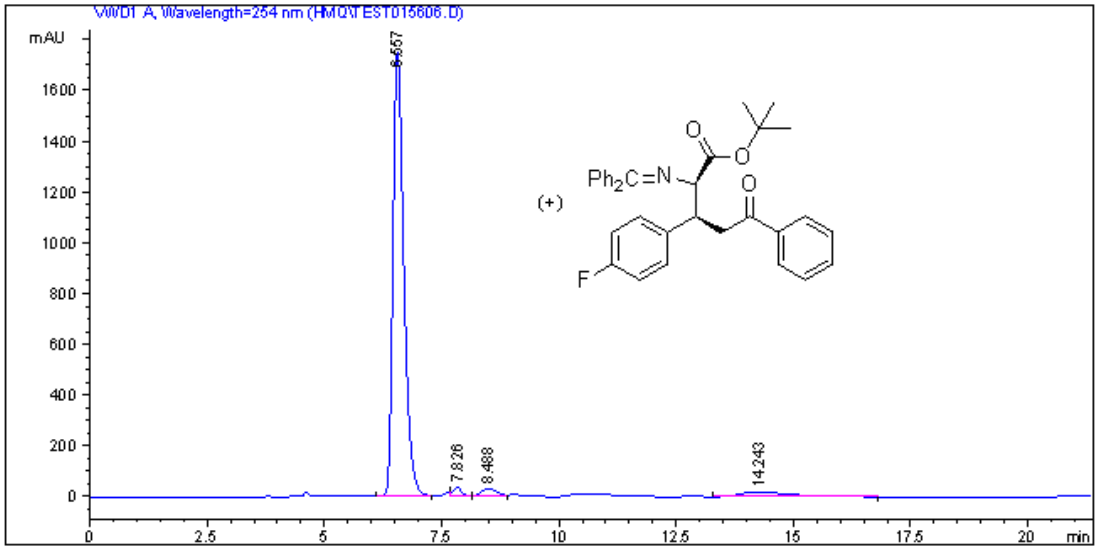
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.014	VB	0.6596	3.75097e4	866.06055	89.8518
2	34.663	VV	0.7449	648.54541	13.47726	1.5535
3	35.572	VV	1.0498	1263.17358	17.72588	3.0258
4	37.485	VB	1.0310	2324.74316	34.10902	5.5688
Totals :				4.17461e4	931.37271	



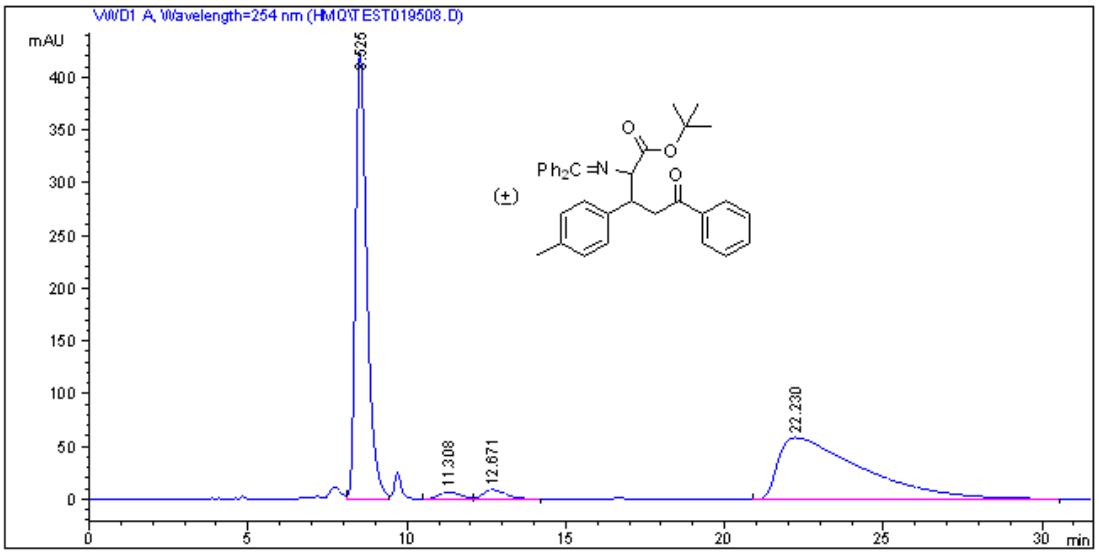
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.553	BBA	0.2384	5996.61816	382.11124	46.5679
2	7.540	BV	0.3068	446.20929	22.24915	3.4651
3	8.461	VV	0.3828	448.91202	17.72485	3.4861
4	13.483	BB	1.1597	5985.41504	75.11106	46.4809



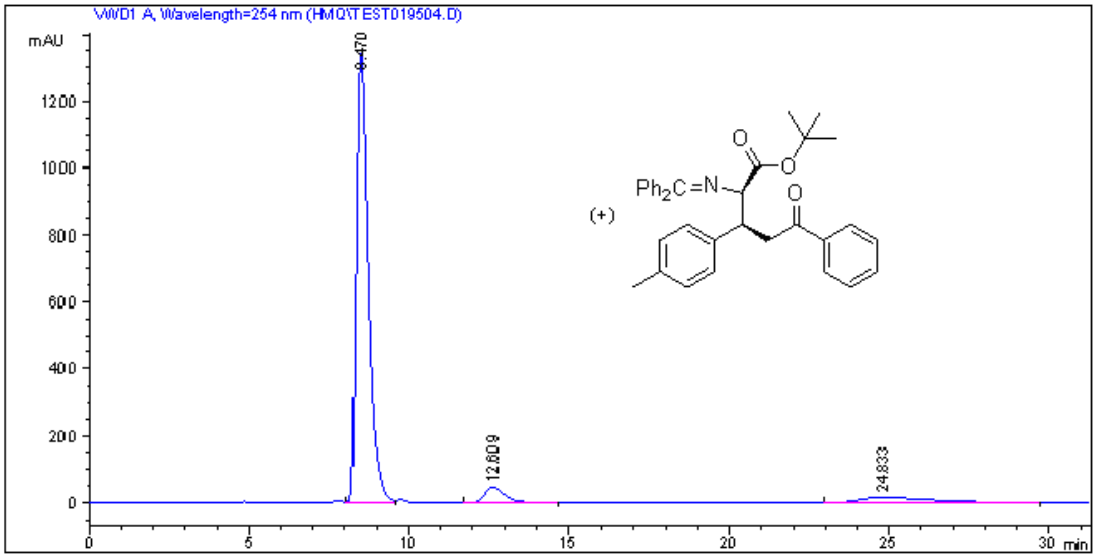
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.557	VV	0.2469	2.83201e4	1751.47644	91.3599
2	7.826	VV	0.1810	488.61374	39.03368	1.5763
3	8.488	VV	0.3674	782.26178	32.59212	2.5236
4	14.243	VBA	1.1068	1407.42529	18.78976	4.5403



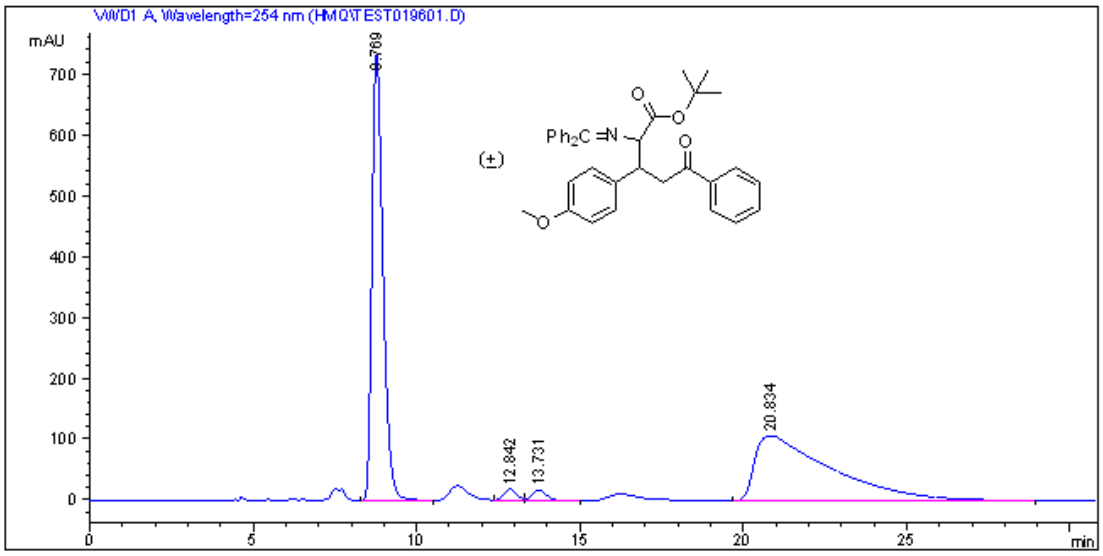
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.525	VBA	0.3820	1.05452e4	421.70993	48.1343
2	11.308	BV	0.7038	298.97260	6.52066	1.3647
3	12.671	VB	0.7780	423.57214	8.78541	1.9334
4	22.230	BB	2.5668	1.06401e4	58.35965	48.5676
Totals :				2.19078e4	495.37565	



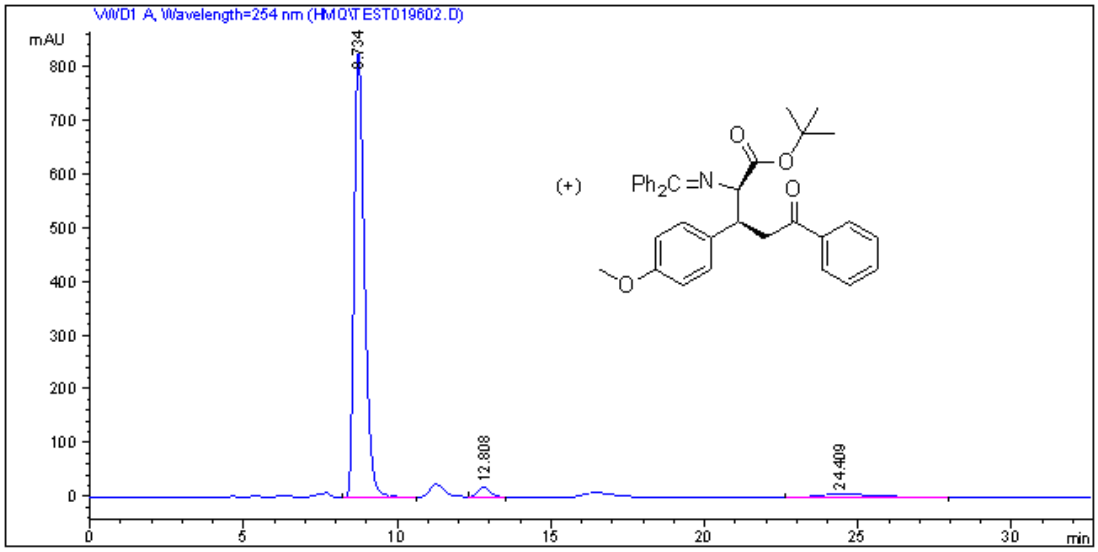
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.470	VV	0.3883	3.42749e4	1341.93127	88.8417
2	12.609	VB	0.6261	1952.19739	46.83176	5.0602
3	24.833	BB	2.0579	2352.63818	15.53568	6.0981
Totals :				3.85797e4	1404.29871	



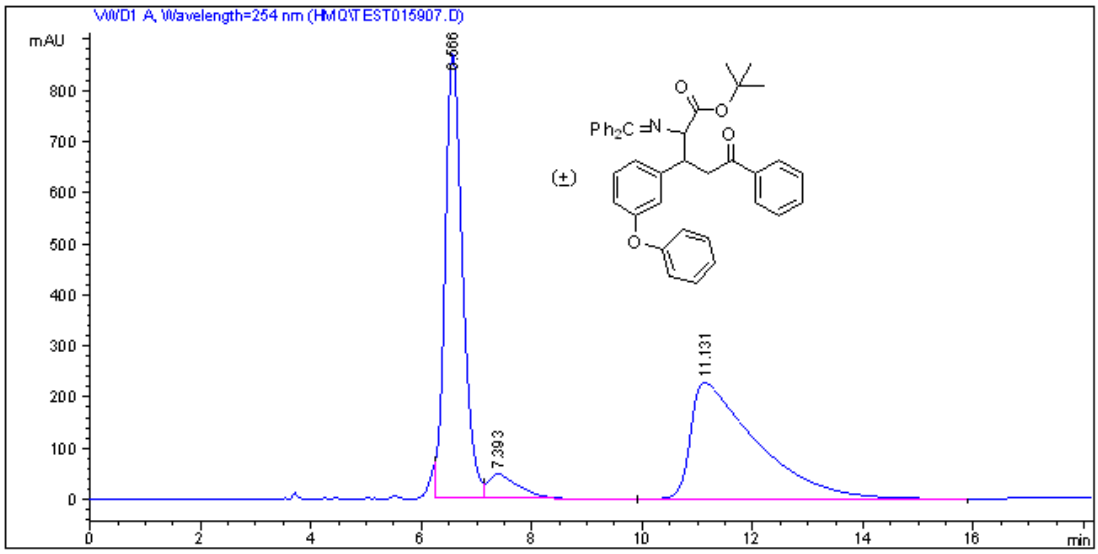
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.769	VBA	0.3620	1.72750e4	733.94446	48.7011
2	12.842	BV	0.4186	485.11447	18.04025	1.3676
3	13.731	VB	0.4551	515.12958	17.44913	1.4522
4	20.834	BB	2.1772	1.71963e4	107.03320	48.4791
Totals :				3.54716e4	876.46704	



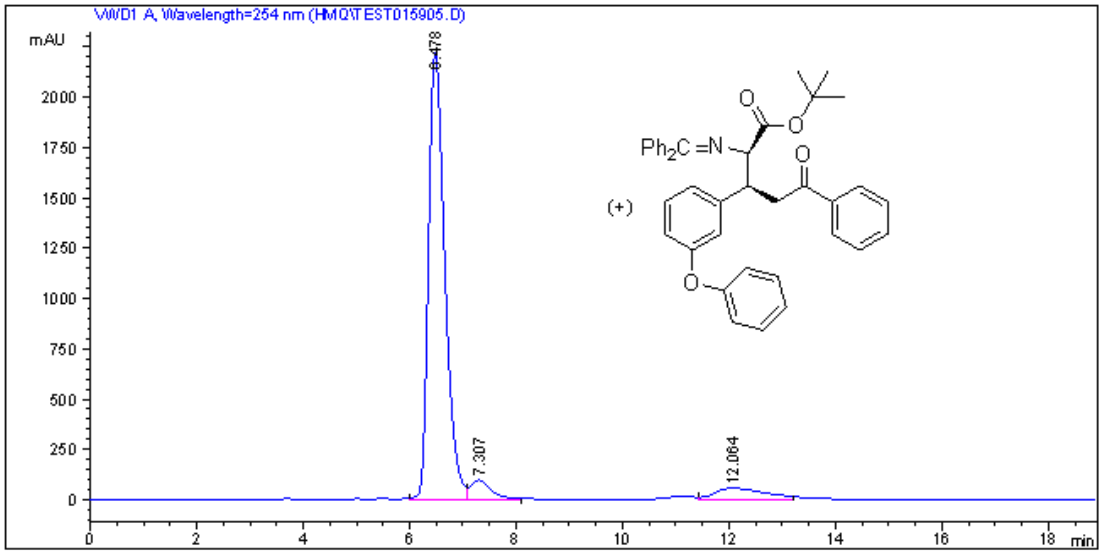
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.734	VV	0.3601	1.93212e4	826.34949	93.6836
2	12.808	BV	0.4236	532.43567	19.31321	2.5817
3	24.409	BB	1.7000	770.23920	6.24946	3.7347
Totals :				2.06238e4	851.91216	



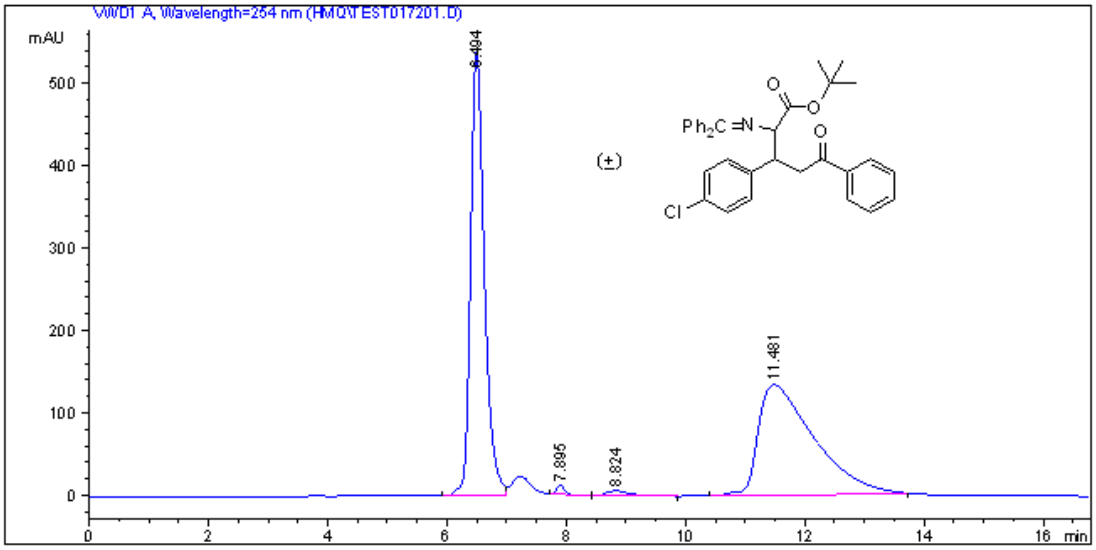
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.566	BV	0.3327	1.91276e4	868.19684	48.1063
2	7.393	VV	0.5013	1743.82324	48.13354	4.3858
3	11.131	VB	1.1520	1.88896e4	227.54025	47.5079
Totals :				3.97610e4	1143.87063	



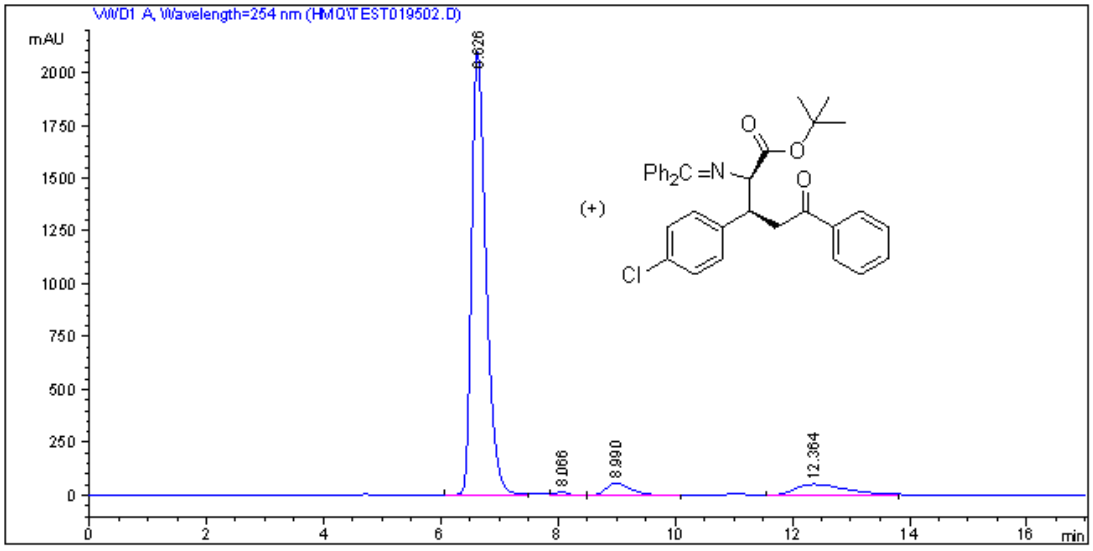
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.478	VV	0.3278	4.73691e4	2218.13989	88.0218
2	7.307	VV	0.3953	2630.88989	96.92289	4.8888
3	12.064	VBA	1.0022	3815.16650	56.99771	7.0894
Totals :				5.3815le4	2372.06049	



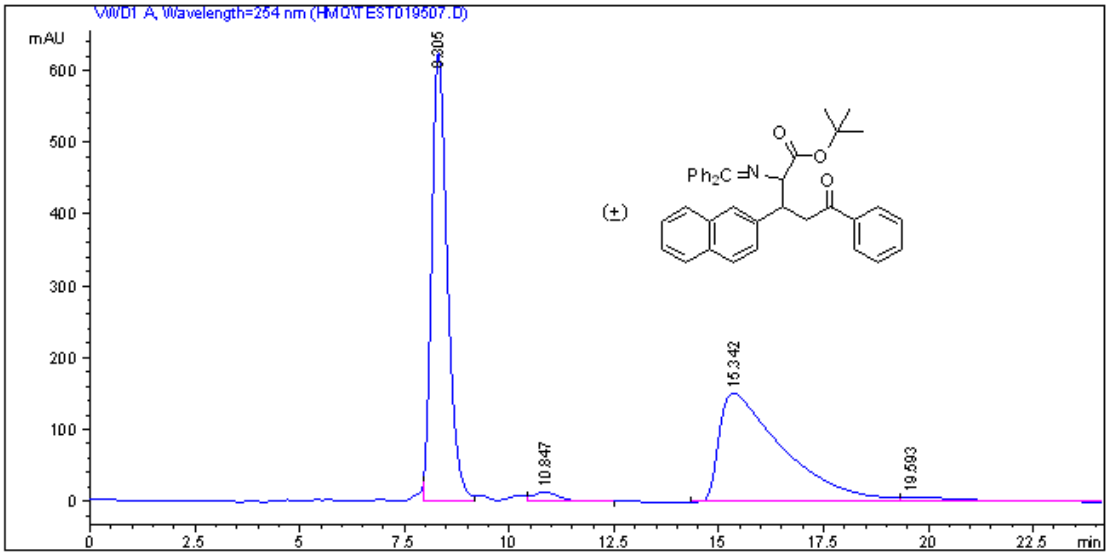
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.494	VBA	0.2469	8719.17187	539.16956	49.1664
2	7.895	BV	0.1430	96.75677	10.73397	0.5456
3	8.824	VV	0.4089	164.02328	6.11796	0.9249
4	11.481	VBA	0.9691	8754.05566	133.96846	49.3631



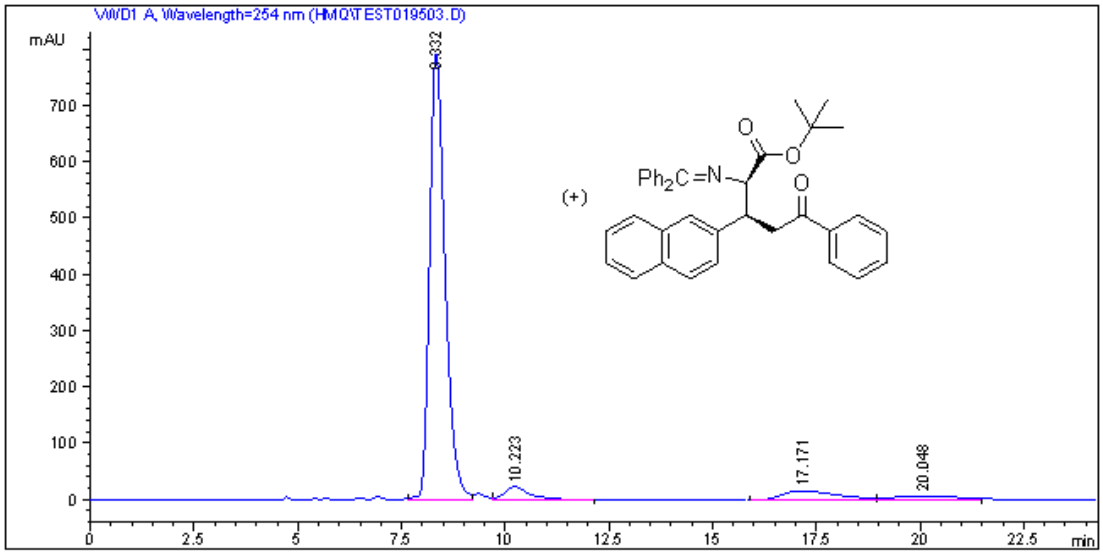
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.626	VV	0.2647	3.60430e4	2095.97388	87.2983
2	8.066	VV	0.2118	254.91852	17.10040	0.6174
3	8.990	VV	0.4372	1708.31287	57.93135	4.1376
4	12.364	VBA	0.9541	3280.92261	52.02935	7.9466
Totals :				4.12872e4	2223.03498	



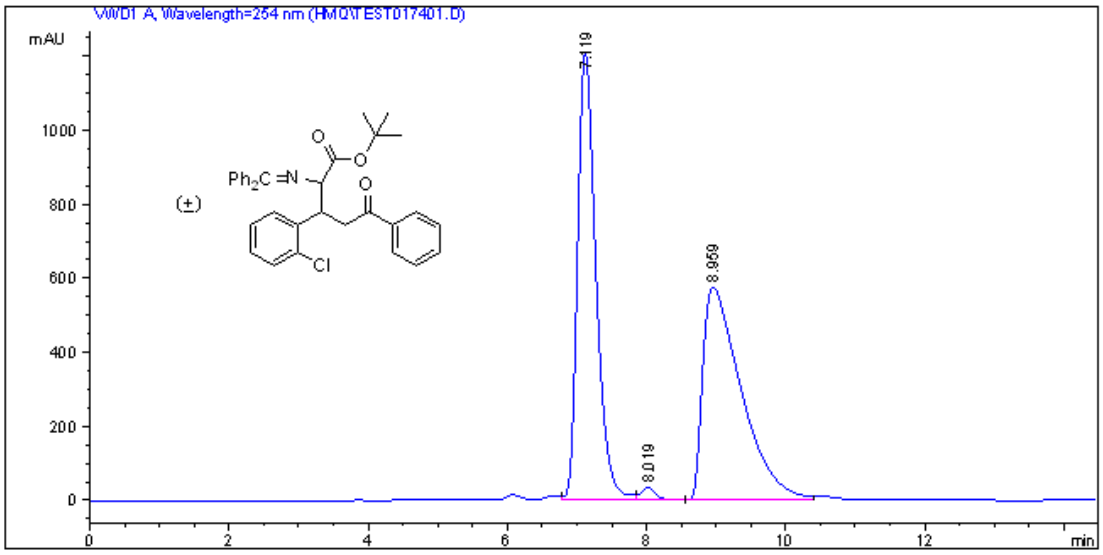
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.305	BV	0.3954	1.63647e4	625.63080	48.5634
2	10.847	VV	0.6613	613.48279	13.64758	1.8206
3	15.342	BB	1.4905	1.6069le4	151.54115	47.6865
4	19.593	BBA	1.2685	650.20966	6.22297	1.9295



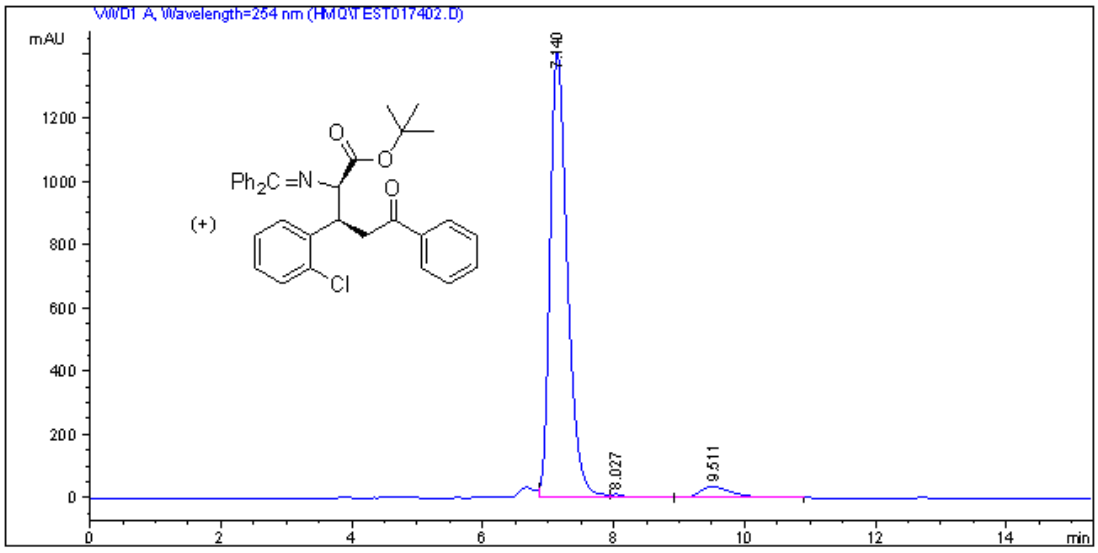
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.332	VV	0.3964	2.06254e4	793.71204	86.3170
2	10.223	VB	0.6420	1013.81250	23.14939	4.2428
3	17.171	VV	1.3751	1477.55444	16.20851	6.1836
4	20.048	VBA	1.4717	778.17010	7.34610	3.2566
Totals :				2.38949e4	840.41604	



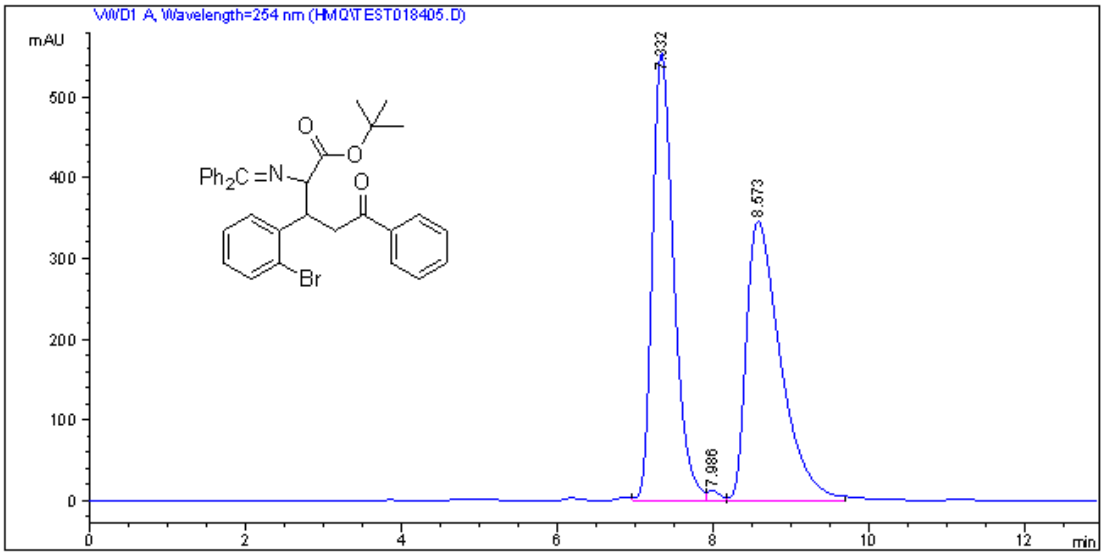
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.119	VV	0.2814	2.22049e4	1208.13550	49.2917
2	8.019	VV	0.2138	552.38226	36.63074	1.2262
3	8.959	VV	0.5961	2.22907e4	577.23853	49.4821
Totals :				4.50480e4	1822.00476	



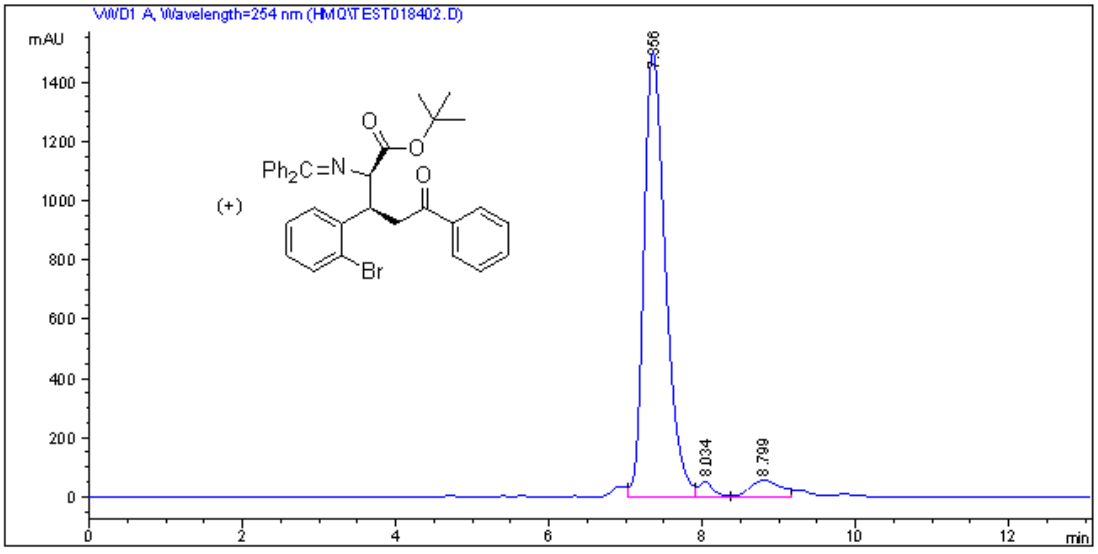
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.140	BV	0.2822	2.59031e4	1404.33374	94.9596
2	8.027	VV	0.2111	162.79120	10.96045	0.5968
3	9.511	VBA	0.5279	1212.12842	34.86501	4.4436
Totals :				2.72780e4	1450.15919	



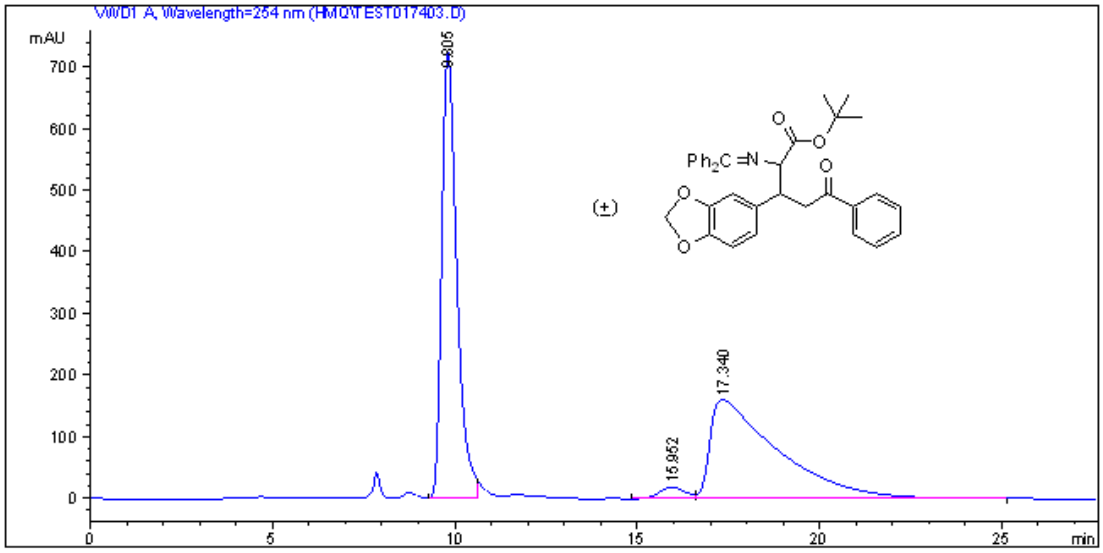
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.332	VV	0.2930	1.05947e4	554.08124	49.7068
2	7.986	VV	0.1710	143.53465	12.30884	0.6734
3	8.573	VBA	0.4642	1.0576le4	346.19043	49.6198
Totals :				2.13144e4	912.58050	



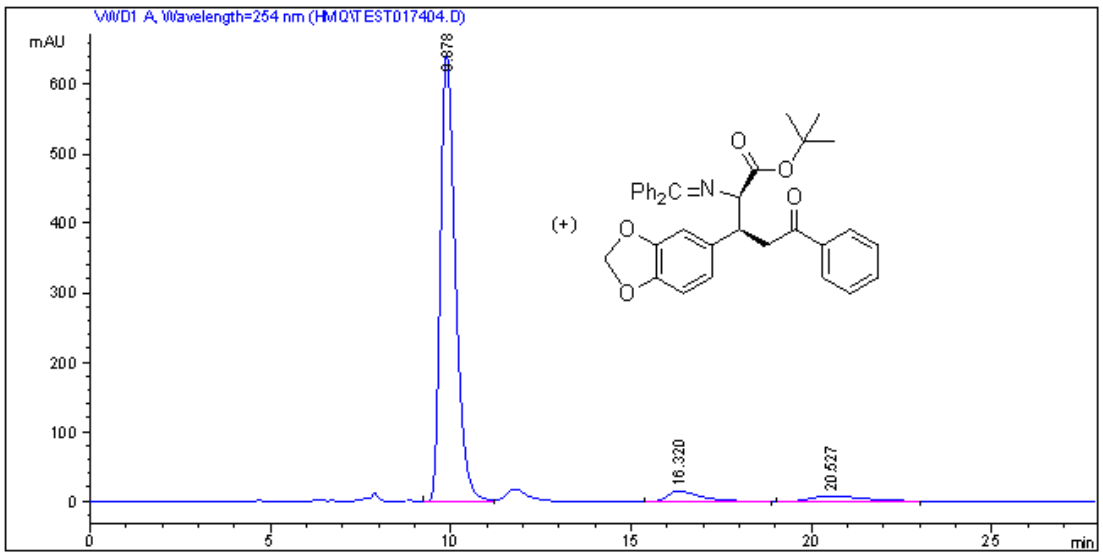
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.356	VV	0.2980	2.93257e4	1500.04626	92.7057
2	8.034	VV	0.1959	716.55371	52.88936	2.2652
3	8.799	VBA	0.4326	1590.85498	56.62020	5.0291
Totals :				3.16331e4	1609.55583	



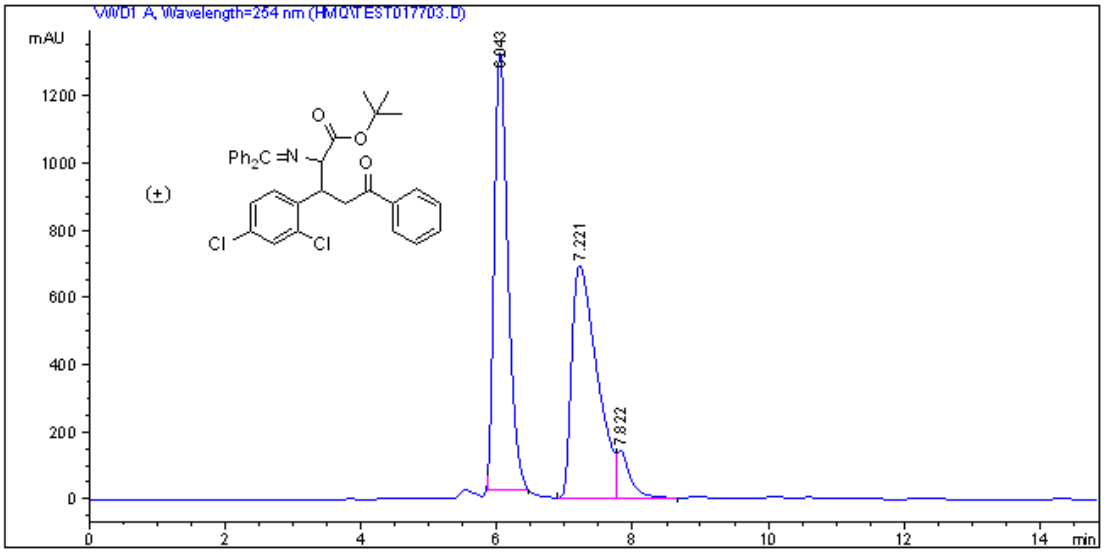
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.805	VBA	0.4382	2.08821e4	724.40387	49.0565
2	15.952	VV	0.7799	904.78900	18.13997	2.1255
3	17.340	VB	1.7661	2.07805e4	160.26247	48.8179
Totals :				4.25674e4	902.80630	



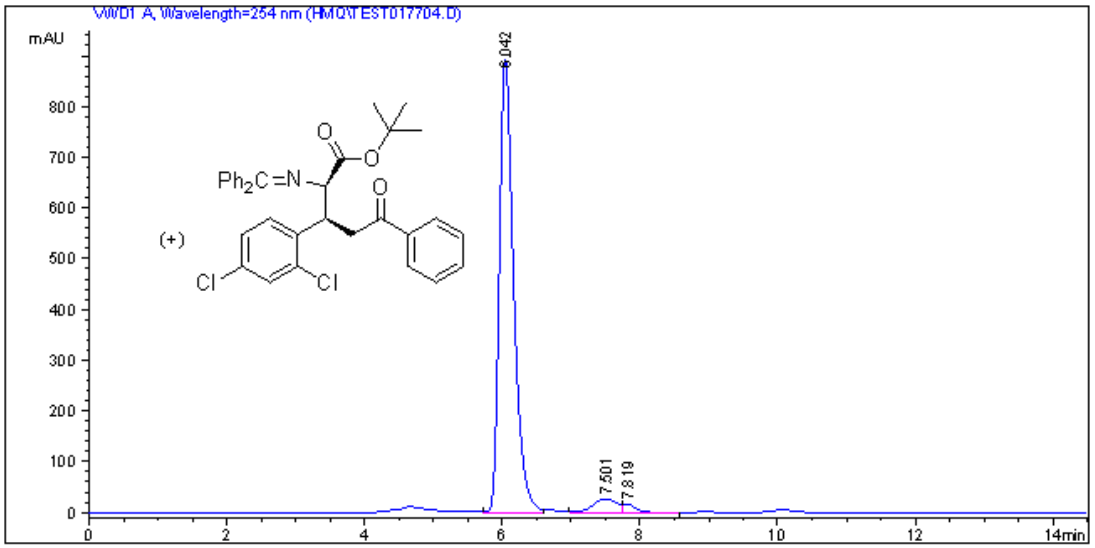
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.878	VV	0.4428	1.86365e4	643.42371	91.0944
2	16.320	BB	0.8972	982.48517	15.67514	4.8023
3	20.527	BBA	1.4990	839.46356	7.84427	4.1033
Totals :				2.04584e4	666.94312	



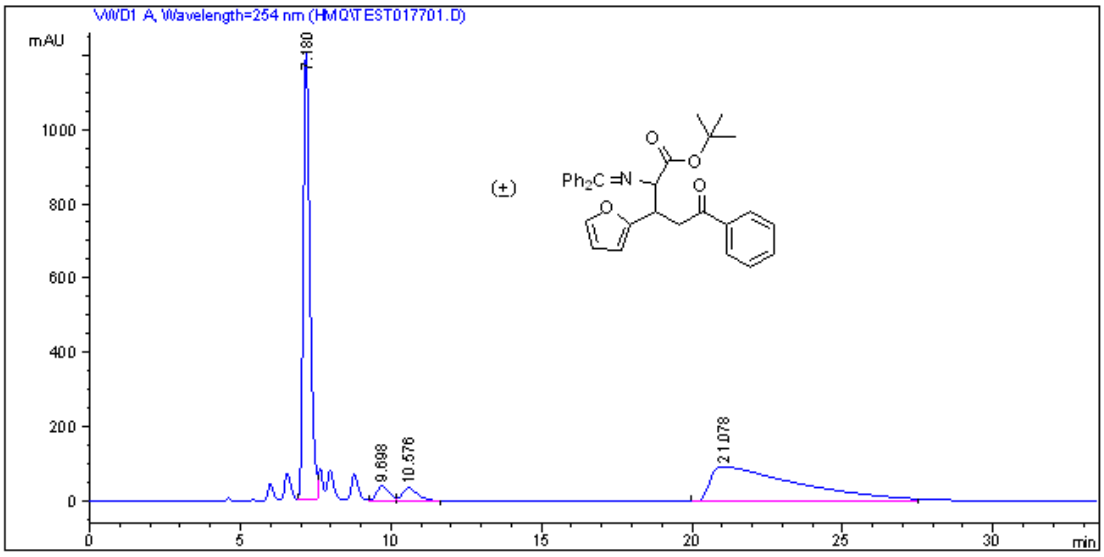
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.043	BBA	0.2149	1.81331e4	1301.75061	47.7088
2	7.221	BV	0.3915	1.78761e4	692.43280	47.0327
3	7.822	VV	0.1954	1998.67505	142.71268	5.2586
Totals :				3.80079e4	2136.89609	



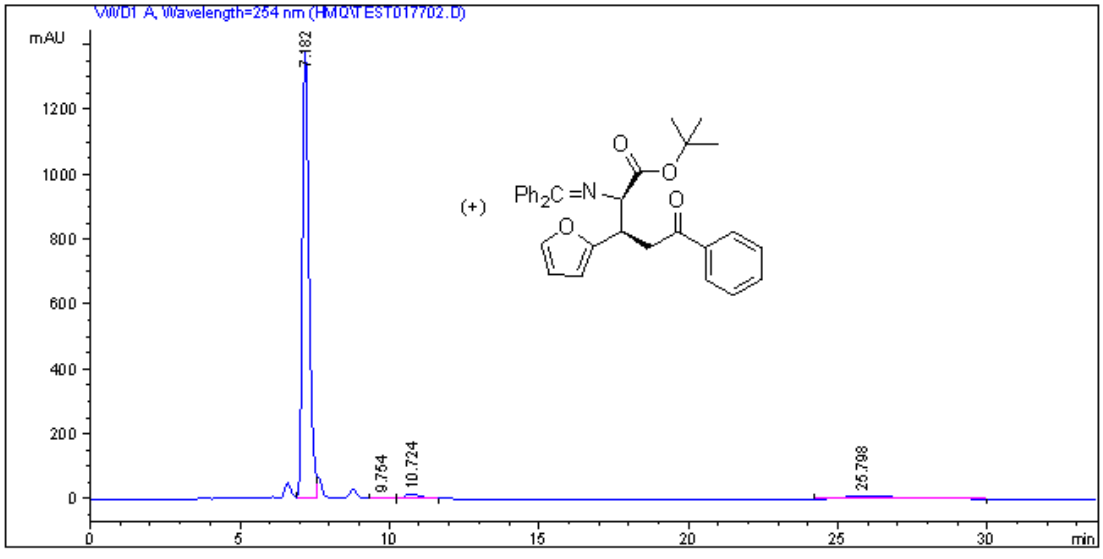
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.042	VV	0.2187	1.29661e4	894.17065	93.2055
2	7.501	VV	0.4007	694.63715	27.38734	4.9933
3	7.819	VV	0.1990	250.56900	17.81872	1.8012
Totals :				1.39113e4	939.37672	



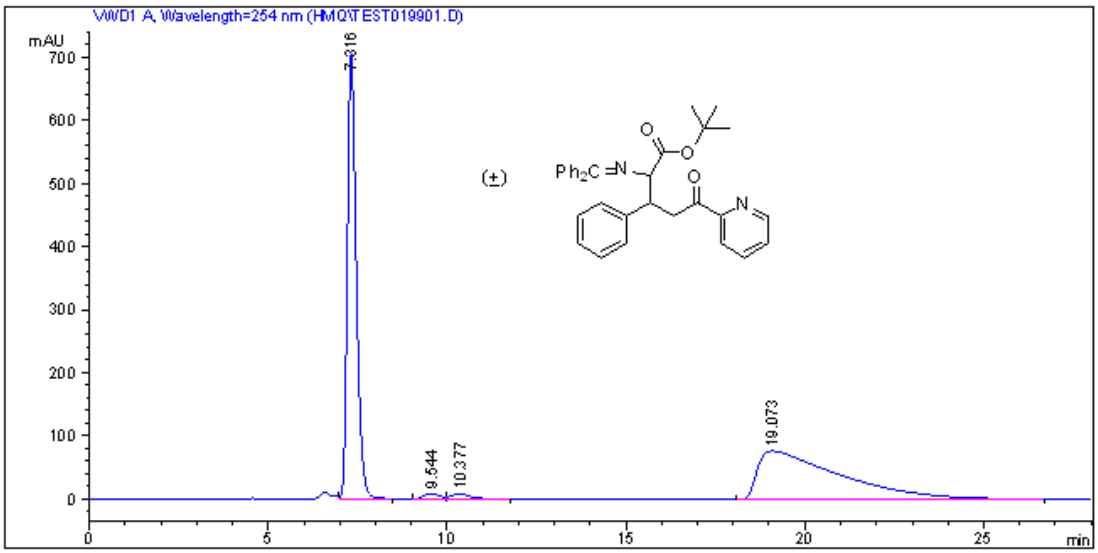
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.180	BV	0.2357	1.85352e4	1198.77820	46.9936
2	9.698	VV	0.4347	1053.33228	37.59023	2.6706
3	10.576	VV	0.5275	1182.66675	34.05288	2.9985
4	21.078	BBA	2.7340	1.86708e4	91.34817	47.3373
Totals :				3.94420e4	1361.76948	



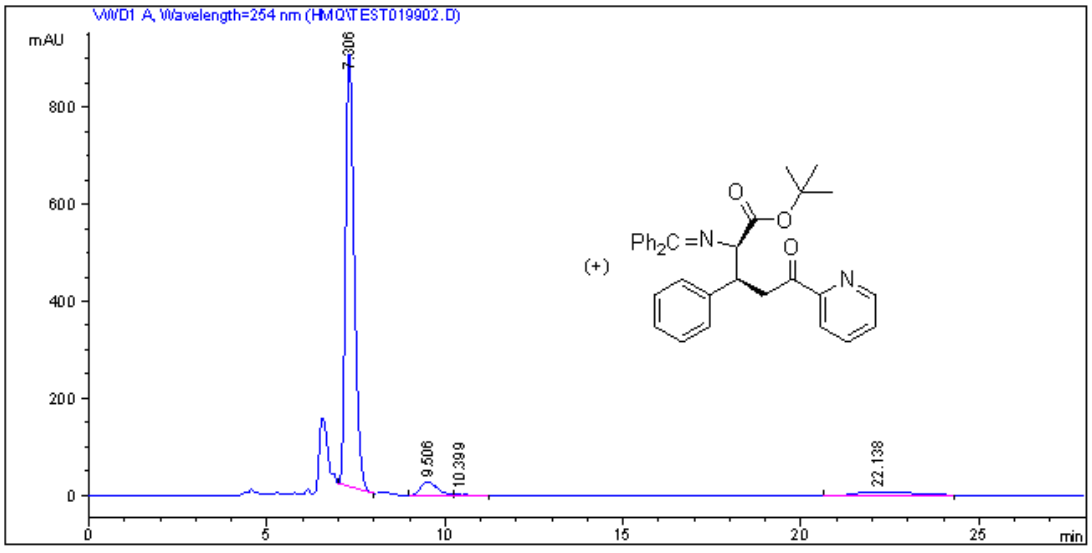
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.182	BV	0.2398	2.13417e4	1371.27734	92.5832
2	9.754	BV	0.3847	51.57313	2.12762	0.2237
3	10.724	VV	0.5275	521.52295	15.12486	2.2624
4	25.798	BB	1.7632	1136.58972	8.59979	4.9307



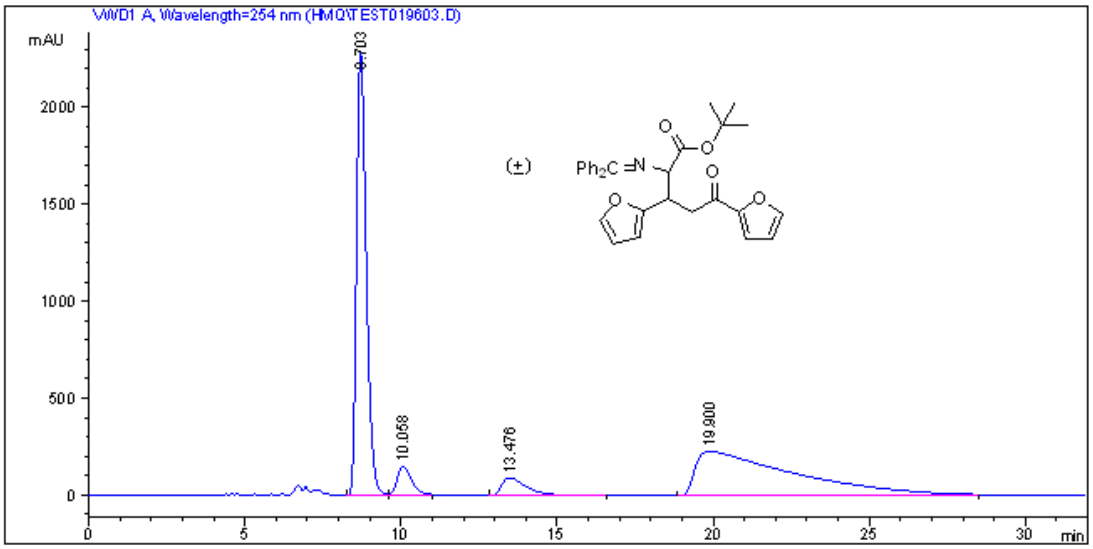
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.316	VV	0.2673	1.23028e4	706.23834	49.1220
2	9.544	VV	0.4738	282.81067	9.23348	1.1292
3	10.377	VB	0.5714	336.54373	8.68573	1.3437
4	19.073	BB	2.1860	1.21233e4	76.40735	48.4051
Totals :				2.50454e4	800.56490	



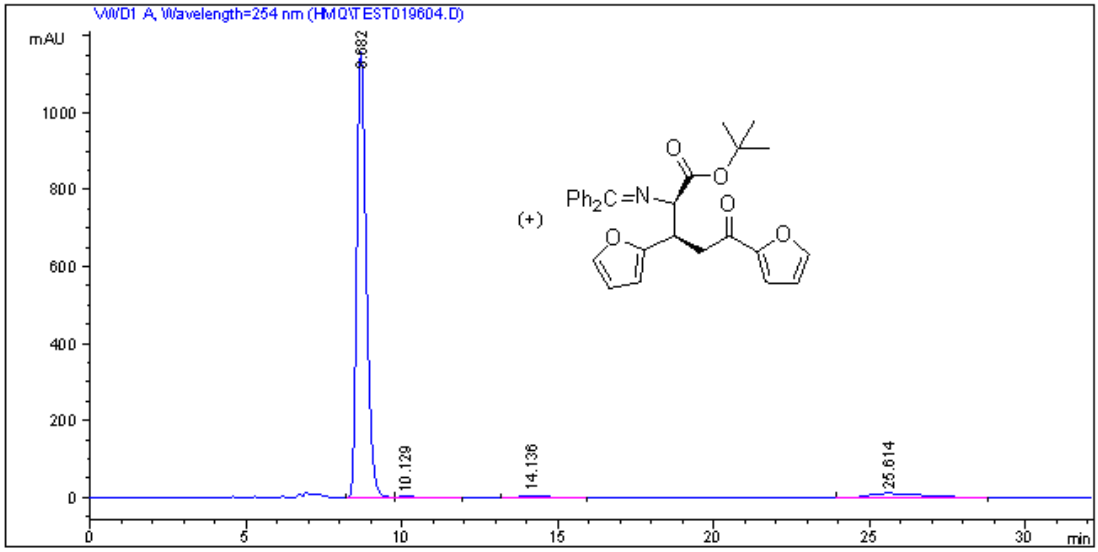
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.306	VV	0.2610	1.50860e4	893.59448	88.6019
2	9.506	VV	0.5046	890.00354	27.37225	5.2271
3	10.399	VV	0.3064	84.95107	3.90174	0.4989
4	22.138	BBA	1.6860	965.77838	8.54176	5.6721
Totals :				1.70268e4	933.41024	



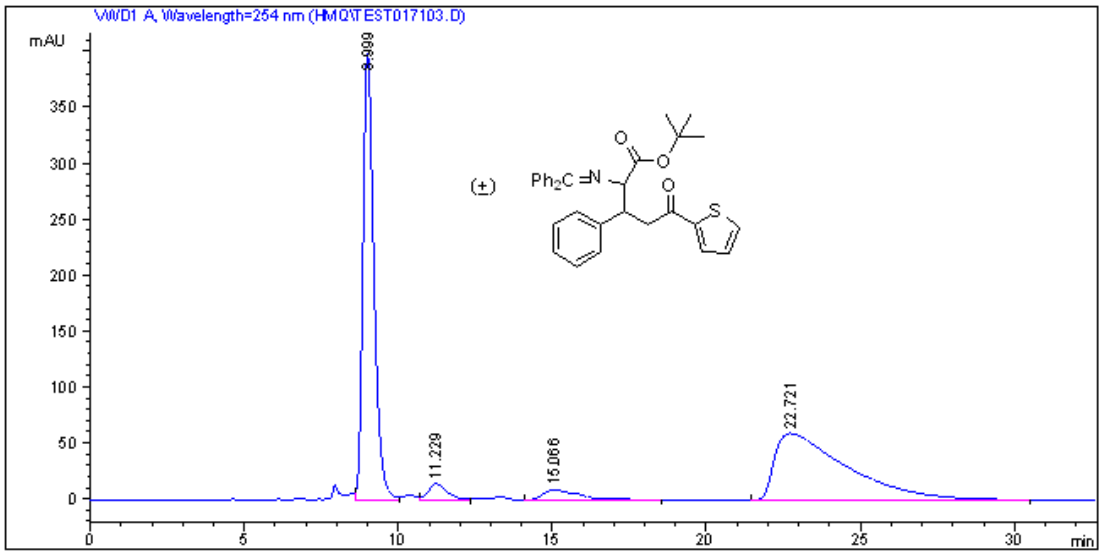
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.703	VV	0.3343	4.94305e4	2281.17285	45.5083
2	10.058	VBA	0.4891	4853.96924	150.80789	4.4688
3	13.476	BB	0.8116	4841.74854	90.34537	4.4576
4	19.900	BBA	2.9111	4.94926e4	224.89774	45.5654
Totals :				1.08619e5	2747.22385	



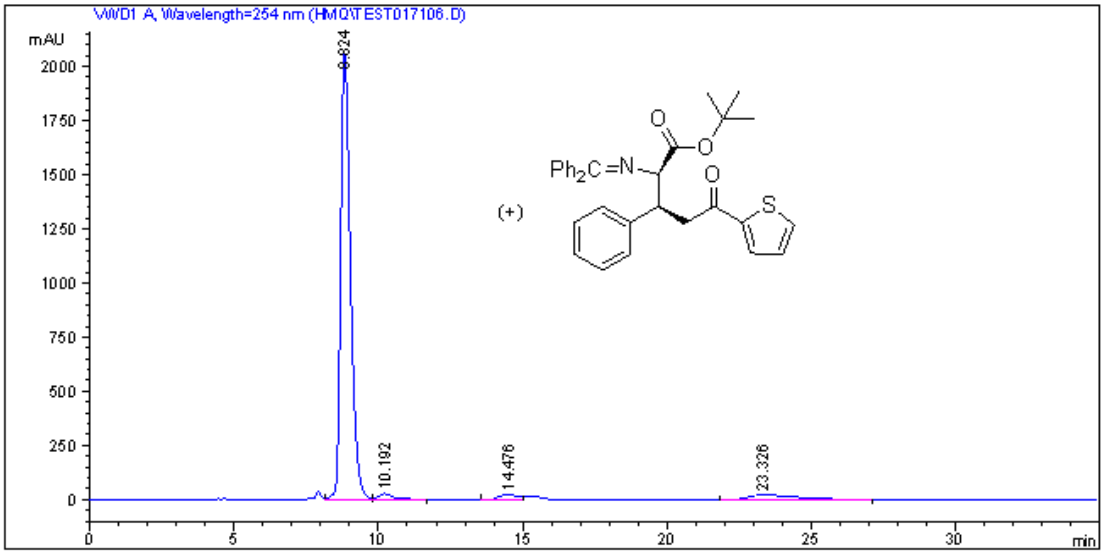
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.682	BV	0.3264	2.46013e4	1158.18677	92.8335
2	10.129	VB	0.5809	132.27531	3.28140	0.4991
3	14.136	BB	0.8257	333.77219	6.06288	1.2595
4	25.614	BBA	1.8900	1433.11682	11.25727	5.4079
Totals :				2.65004e4	1178.78832	



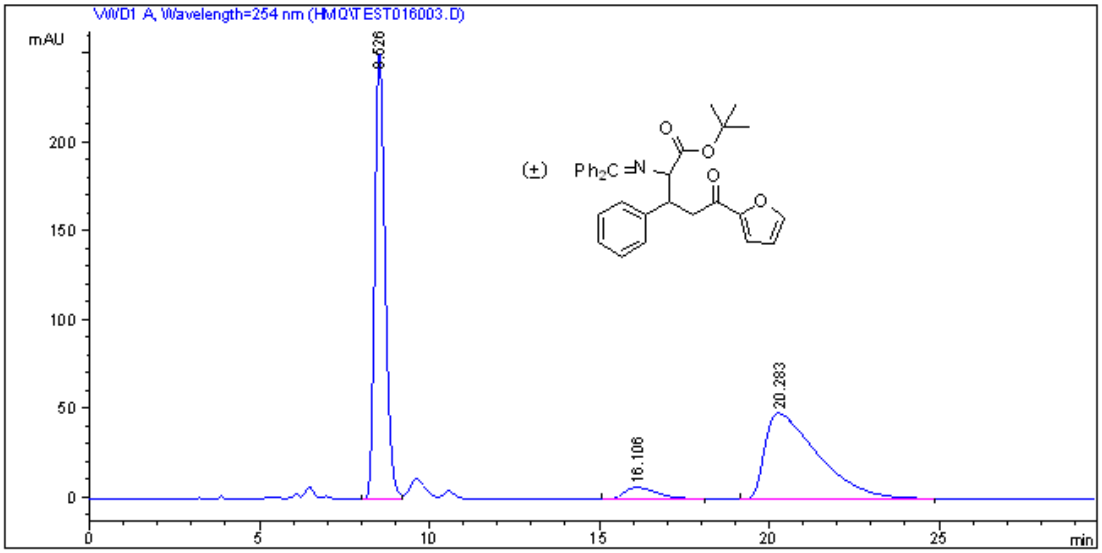
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.999	BV	0.3803	9908.89551	398.56277	47.0058
2	11.229	VV	0.6498	638.13483	14.68166	3.0272
3	15.066	VB	1.1763	797.85291	9.40262	3.7849
4	22.721	BB	2.2528	9735.26465	59.67287	46.1821
Totals :				2.10801e4	482.31992	



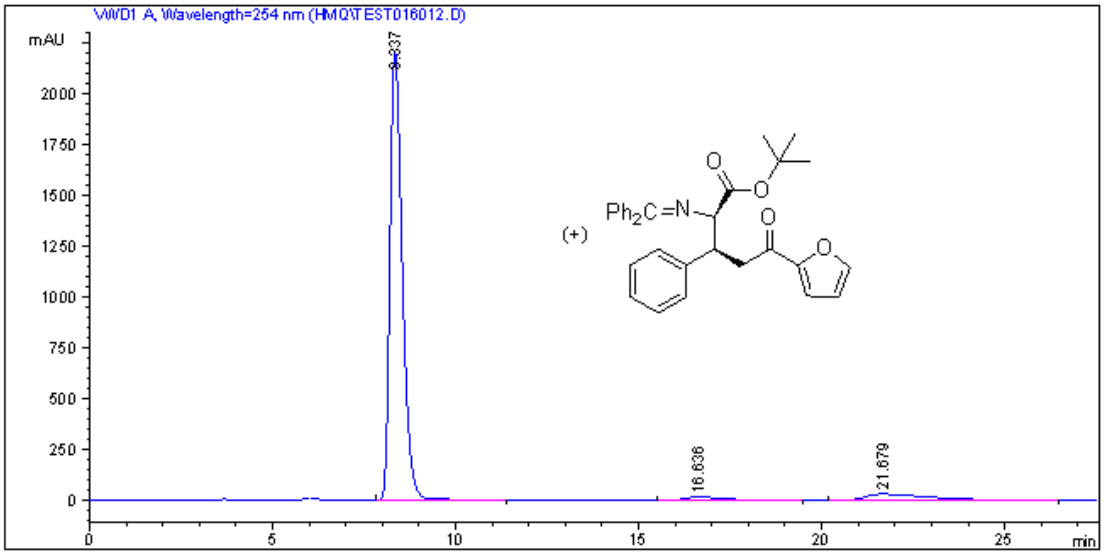
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.824	VV	0.3610	4.89067e4	2063.07080	90.7641
2	10.192	VV	0.5525	1080.23364	28.15181	2.0048
3	14.476	VV	0.7327	1096.55347	23.29380	2.0351
4	23.326	BBA	1.8175	2799.79590	22.16162	5.1960
Totals :				5.38832e4	2136.67803	



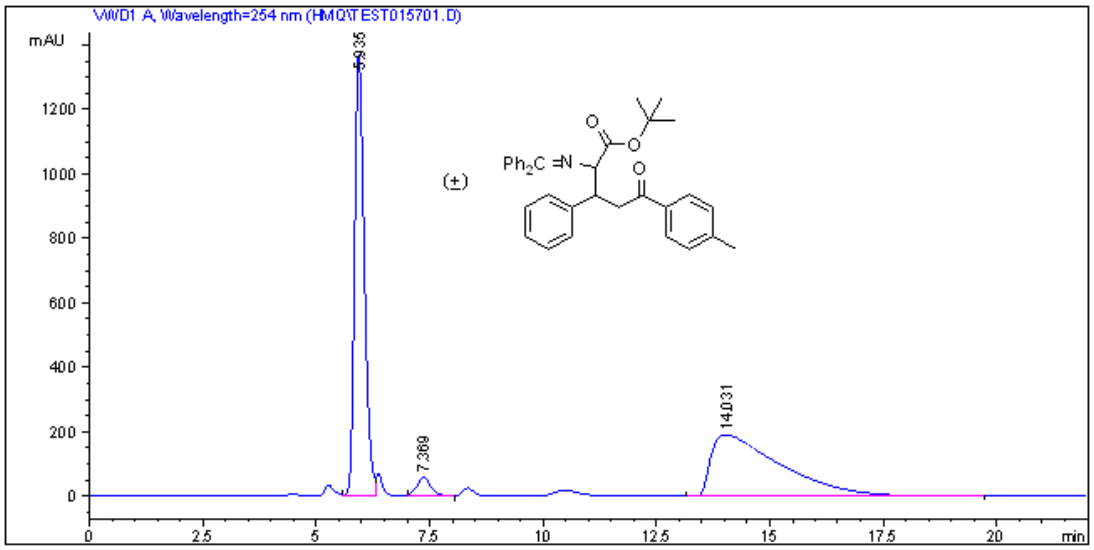
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.526	VV	0.3266	5345.30664	251.46826	48.5425
2	16.106	BB	1.0494	428.07056	6.34285	3.8875
3	20.283	BB	1.5454	5238.21436	48.27937	47.5700
Totals :				1.10116e4	306.09047	



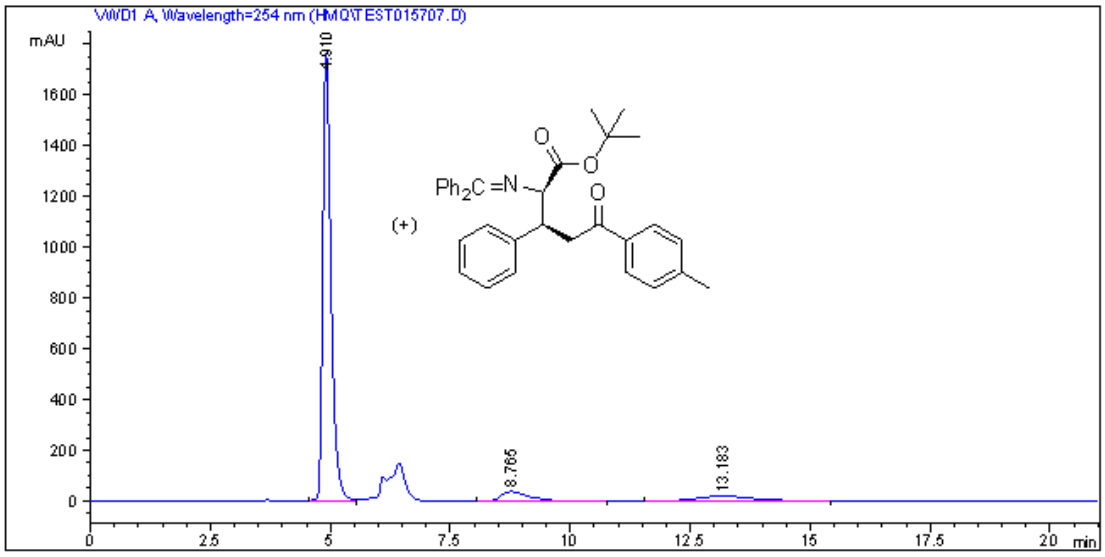
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.337	VB	0.3581	5.16925e4	2203.83447	91.5991
2	16.636	BB	1.1188	1159.09021	15.62423	2.0539
3	21.679	BB	1.7447	3581.83105	29.76369	6.3470
Totals :				5.64335e4	2249.22239	



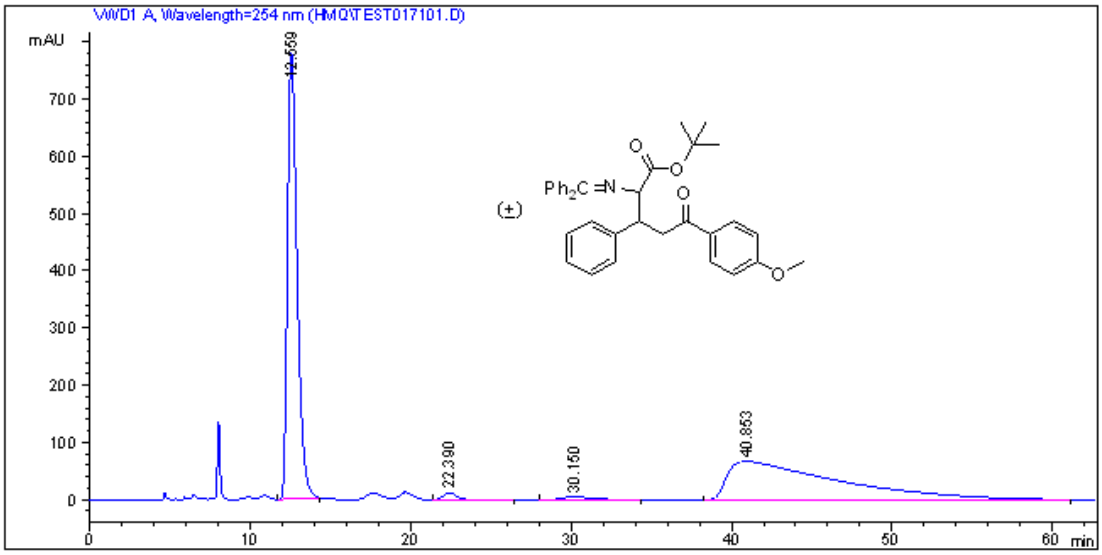
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.935	VV	0.2298	2.05134e4	1371.86792	48.5980
2	7.369	BV	0.3194	1304.91895	59.62043	3.0915
3	14.031	BB	1.5266	2.03920e4	190.77527	48.3105
Totals :				4.22103e4	1622.26362	



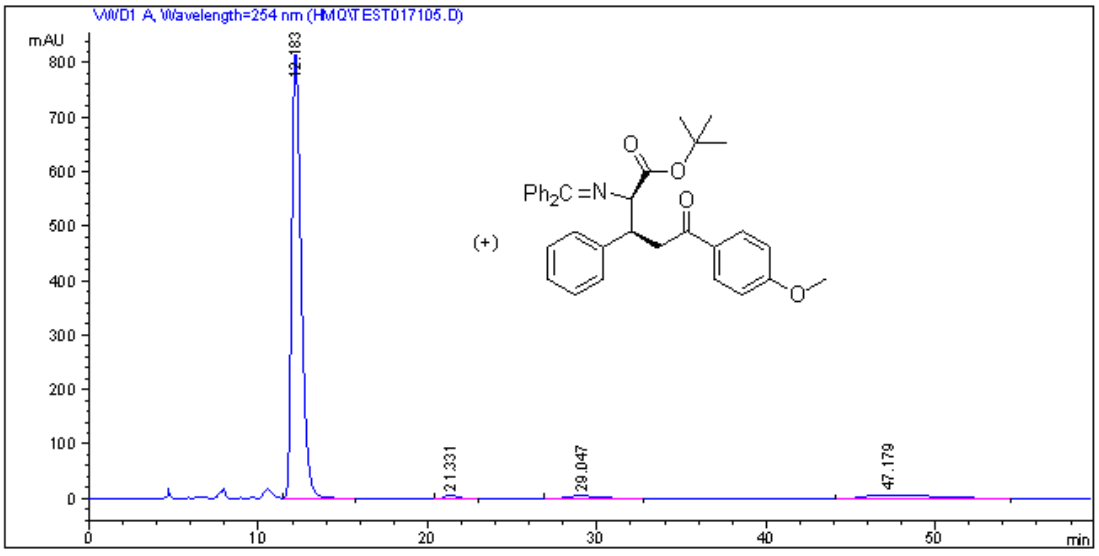
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.910	VV	0.1811	2.12029e4	1763.24304	87.7563
2	8.765	BB	0.6028	1500.90002	37.34822	6.2121
3	13.183	BB	1.2217	1457.30127	18.15881	6.0316
Totals :				2.41611e4	1818.75007	



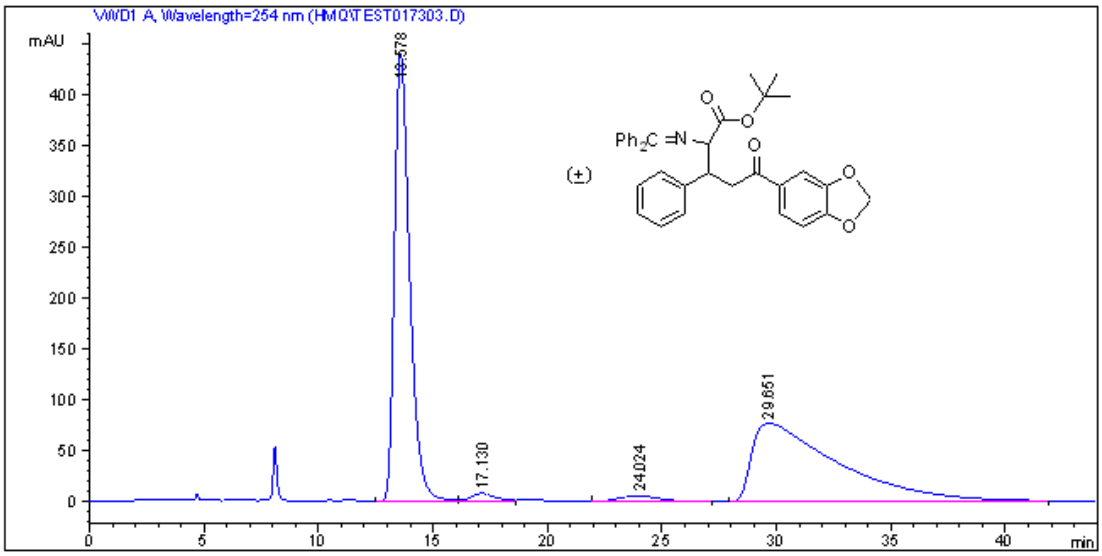
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.559	VBA	0.6386	3.25142e4	778.68781	49.0169
2	22.390	VB	0.8951	706.59784	12.18184	1.0652
3	30.150	BB	1.8707	812.83490	5.30881	1.2254
4	40.853	BB	6.0140	3.22991e4	67.31870	48.6925
Totals :				6.63327e4	863.49714	



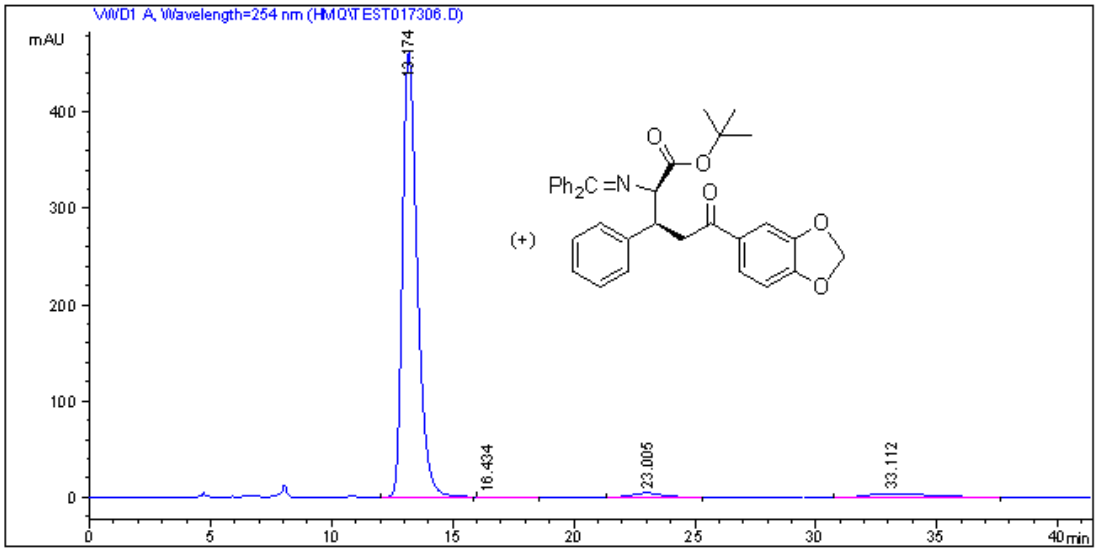
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.183	BB	0.5951	3.16697e4	816.69629	90.6911
2	21.331	BB	0.8220	330.89316	6.04581	0.9476
3	29.047	BB	1.7289	713.80933	5.01983	2.0441
4	47.179	BBA	3.3952	2205.99658	7.67909	6.3172
Totals :				3.49204e4	835.44102	



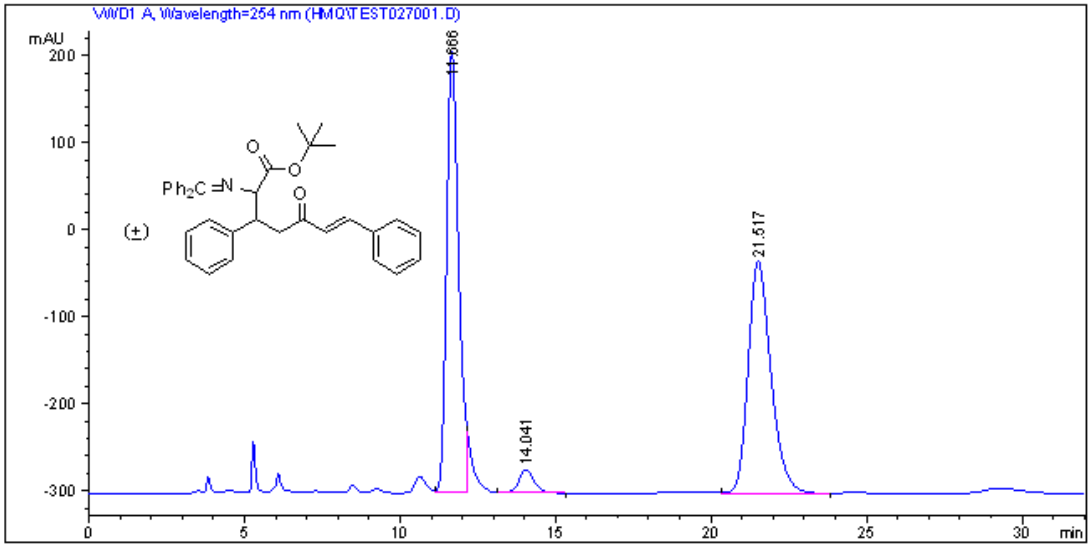
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.578	BV	0.7094	2.03767e4	439.83020	49.1446
2	17.130	VV	1.1211	565.24677	7.59993	1.3633
3	24.024	BB	1.4466	611.12427	5.22308	1.4739
4	29.651	BB	3.4471	1.99097e4	76.49599	48.0182
Totals :				4.14628e4	529.14920	



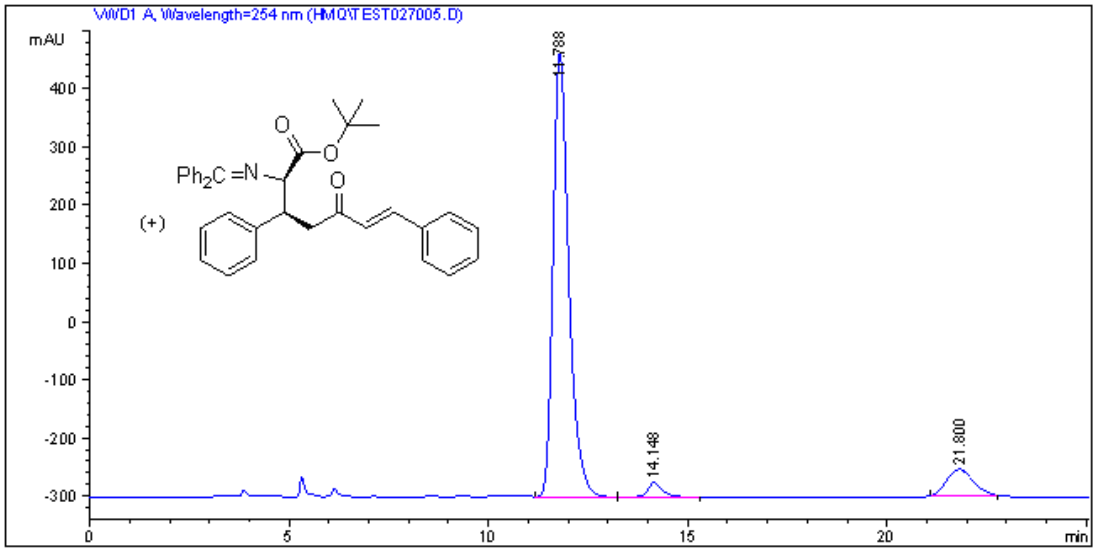
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.174	BB	0.6499	1.96294e4	462.12119	94.3795
2	16.434	BB	0.8638	48.75469	6.76776e-1	0.2344
3	23.005	BB	1.1504	399.68509	4.52266	1.9217
4	33.112	BB	2.0397	720.54321	4.13916	3.4644
Totals :				2.07984e4	471.45978	



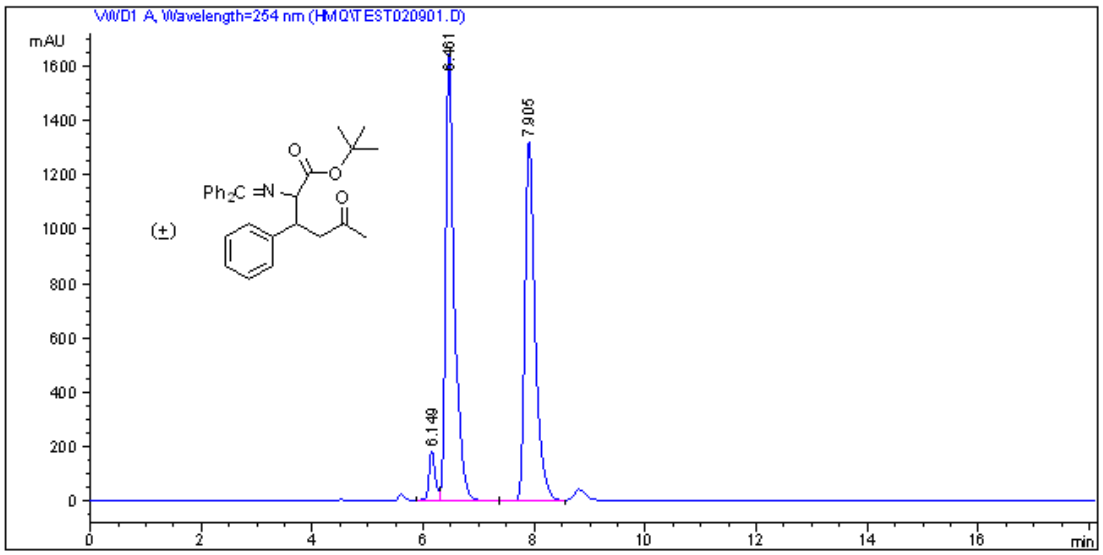
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.666	VBA	0.4080	1.35432e4	506.61539	48.5050
2	14.041	BB	0.5088	881.58838	26.40933	3.1574
3	21.517	VB	0.7762	1.34964e4	265.65402	48.3376
Totals :				2.79212e4	798.67874	



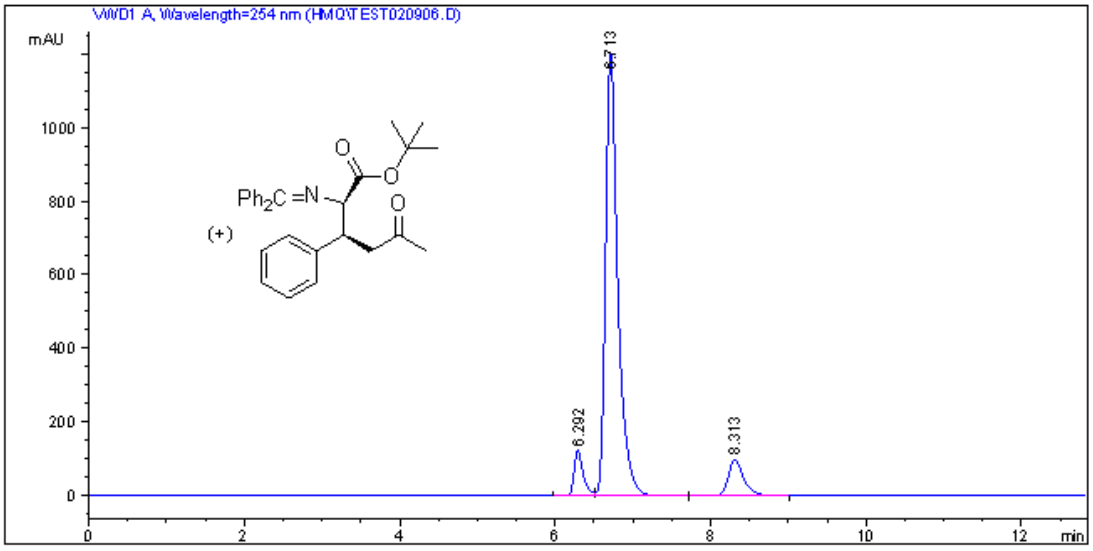
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.788	VV	0.4160	2.09275e4	763.16248	88.6798
2	14.148	VB	0.3554	598.62341	24.46507	2.5367
3	21.800	BBA	0.7233	2072.82446	44.79878	8.7835
Totals :				2.35990e4	832.42632	



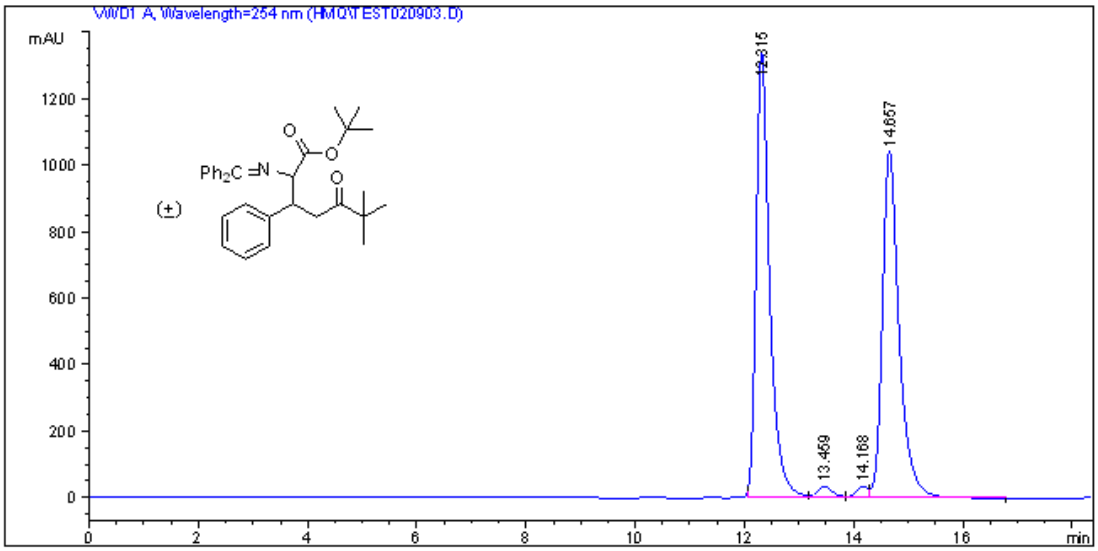
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.149	VV	0.1177	1440.97473	183.82474	4.0386
2	6.461	VBA	0.1547	1.73088e4	1645.54785	48.5112
3	7.905	BV	0.1929	1.69302e4	1324.11755	47.4502
Totals :				3.56800e4	3153.49014	



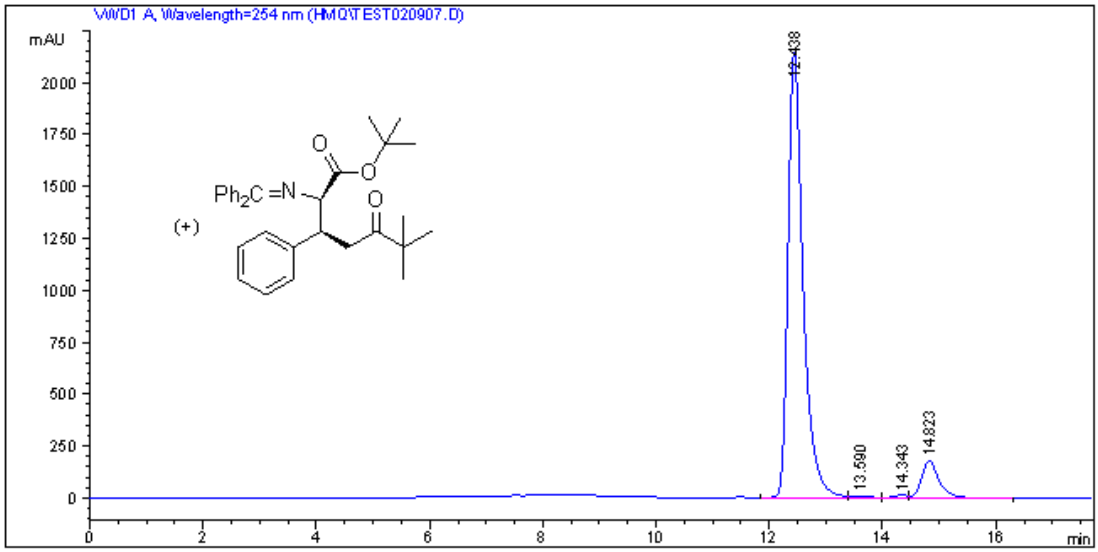
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.292	VV	0.1225	1013.97980	122.90707	6.5030
2	6.713	VV	0.1659	1.31918e4	1202.25427	84.6039
3	8.313	VV	0.2086	1386.64221	99.87807	8.8930
Totals :				1.55924e4	1425.03941	



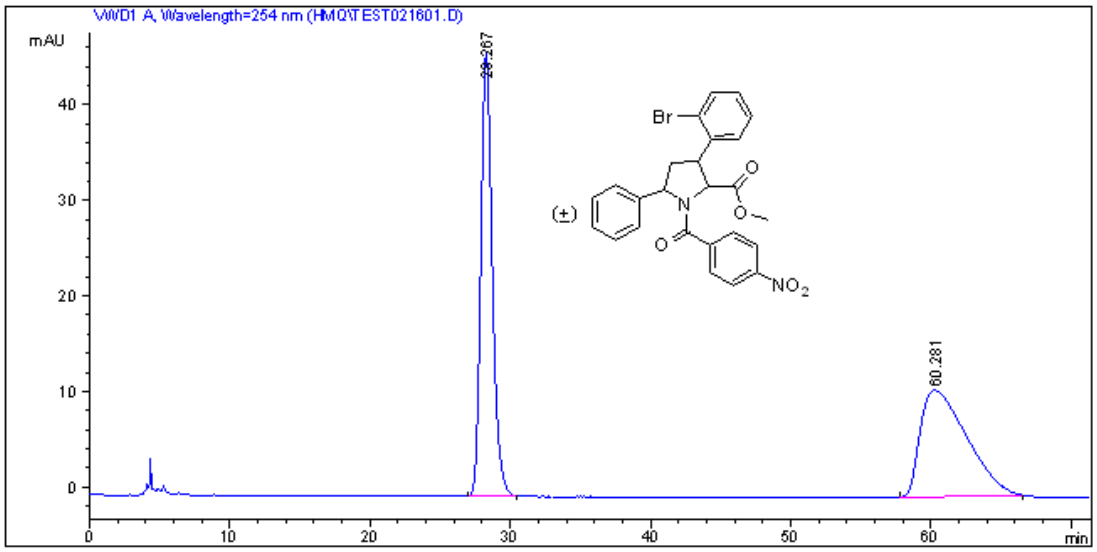
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.315	BV	0.2606	2.32282e4	1338.97925	49.6715
2	13.459	VV	0.3058	735.27258	35.92561	1.5723
3	14.168	VV	0.2365	558.10199	35.93771	1.1935
4	14.657	VB	0.3189	2.2242le4	1042.24854	47.5628



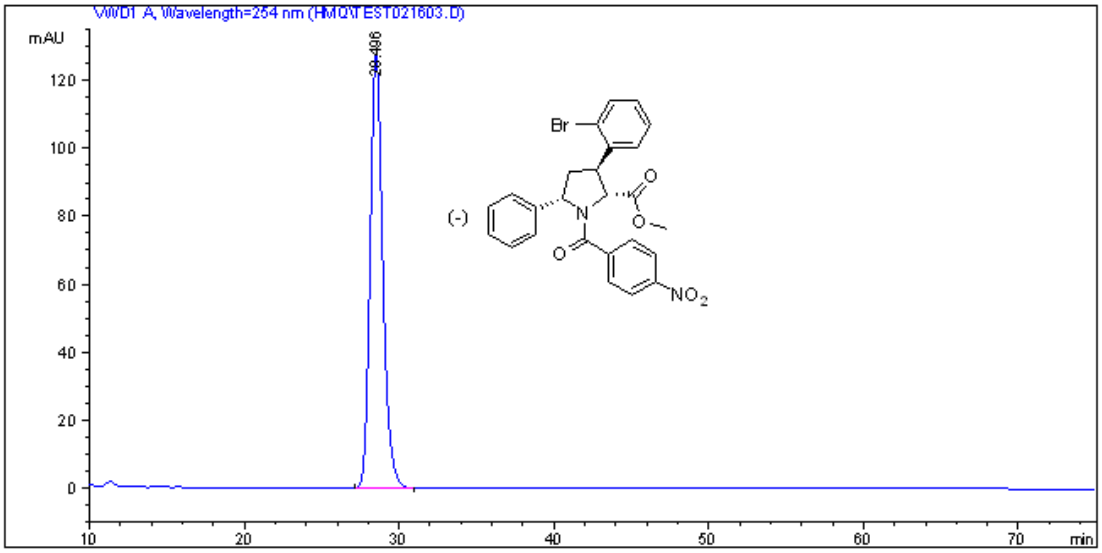
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.438	VV	0.2782	3.99024e4	2144.39429	90.1626
2	13.590	VV	0.3146	234.40588	11.04586	0.5297
3	14.343	VV	0.2598	231.27678	13.38842	0.5226
4	14.823	VB	0.3238	3887.95166	178.61230	8.7851
Totals :				4.42560e4	2347.44087	



Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.267	BB	0.8654	2626.07764	46.31041	50.4529
2	60.281	BB	2.7277	2578.92725	11.14938	49.5471
Totals :				5205.00488	57.45979	

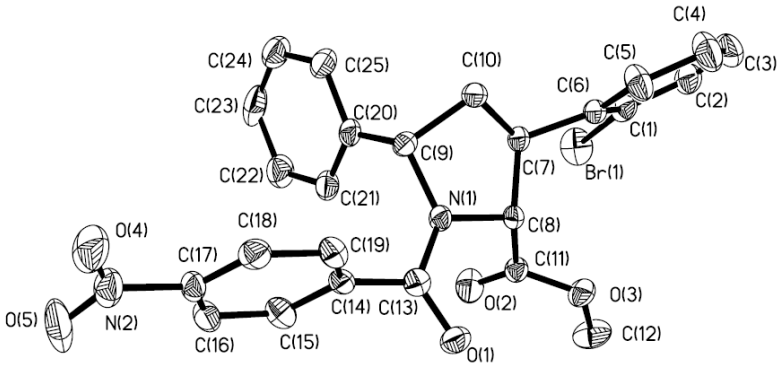


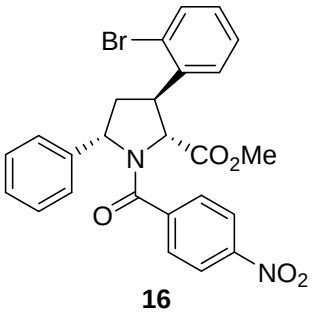
Signal 1: VWD1 A, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	28.496	BB	0.8677	7275.03906	127.84914	100.0000
Totals :				7275.03906	127.84914	

9. X-Ray Analysis for the Amino Acid 16

CCDC 742621 contains the supplementary crystallographic data for the product **16**. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.





16