Supporting Information

Pd-Catalyzed Asymmetric Allylic Alkylations via C-H Activation of *N*-Allyl Imines with Glycinates

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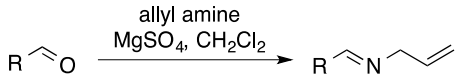
I. General: All reactions were performed in flame- or oven-dried glassware with magnetic stirring under nitrogen or argon atmosphere using freshly distilled solvents. THF was distilled over sodium and CH_2Cl_2 was obtained from a solvent purification system (activated alumina). All commercial reagents were used without purification unless otherwise noted. Air and moisture sensitive liquids and solutions were transferred via stainless steel syringe or cannula and introduced into the reaction vessel through rubber septa. Thin-layer chromatography was performed on EMD silica gel 60 F_{254} plates (0.25 mm); visualization of the developed chromatogram was performed by fluorescence quenching and staining with aqueous ceric ammonium molybdate, *p*-anisaldehyde, or potassium permanganate. Organic solutions were concentrated by rotary evaporation below 40 ºC at *ca.* 25 mm Hg. Chromatographic purification of products was accomplished using forced-flow chromatography on Silicycle silica gel (particle size 0.040-0.063 μm). All isolated and characterized compounds were >95% pure as judged by ^{1}H NMR spectroscopic analysis. Melting points were determined on a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectroscopy were performed on a Varian Mercury NMR operating at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm relative to the residual protiated solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.26 ppm); all ^{13}C NMR spectra are proton decoupled. Data for ^{1}H are reported in terms of chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet), coupling constant, and integration; data for ^{13}C are reported in terms of chemical shift. Infrared spectroscopic data was recorded as thin films on sodium chloride plates on a Thermo Scientific Nicolet IR100 FT-IR spectrometer. High-resolution mass spectrometry (HRMS) was measured on a Bruker micrOTOF-Q II electronspray ionization (ESI) mass spectrometer by the Vincent Coates Foundation Mass Spectrometry Laboratory at Stanford University. Mass peaks are reported in *m*/*z* units.

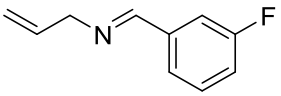
II. Preparation of starting materials:

Imines: Imines **1a**, **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1k**, **1l**, **1m**,**1p** and **1q** were prepared according to the reported literature.[1]

General method for synthesis of imines:

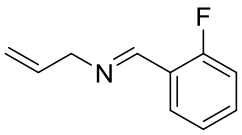


To a stirred solution of aldehyde (10.0 mmol, 1.0 equiv.) in CH_2Cl_2 (12 mL) was added $MgSO_4$ (1.0 g) followed by allyl amine (0.82 mL, 628 mg, 11.0 mmol, 1.1 equiv.). After 24 h, the reaction was filtered through a sintered glass funnel. Solvent was removed *in vacuo*, and the residue was kept under high vacuum for 3 h. The crude material was sufficiently clean (>95% purity by NMR) and was directly used for oxidative C-H activation.



(*E*)-*N*-allyl-1-(3-fluorophenyl)methanimine (1i)

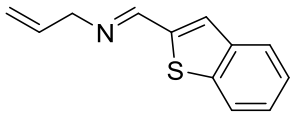
colorless oil. IR: (neat) 3076, 2823, 1648, 1586 cm^{-1}; ^1H NMR (500 MHz, d-$CDCl_3$) δ 8.27 (s, 1H), 7.47-7.52 (m, 2H), 7.35-7.40 (m, 1H), 7.11 (tdd, *J* = 8.5, 3.0, 1.0 Hz, 1H), 6.02-6.10 (m, 1H), 5.24 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.17 (dd, *J* = 10.0, 1.5 Hz, 1H), 4.26 (dd, *J* = 5.5, 1.5 Hz, 2H). ^{13}C NMR (125 MHz, d-$CDCl_3$) δ 163.2 (d, *J* = 245 Hz), 160.8, 138.7 (d, *J* = 7.1 Hz), 135.8, 130.3 (d, *J* = 7.6 Hz), 124.5, 117.9 (d, *J* = 25.1 Hz), 116.5, 114.4 (d, *J* = 22 Hz), 63.6. HRMS (ESI+) calcd. for C10H10FN [M+H] 164.0797, found 164.0795.



(*E*)-*N*-allyl-1-(2-fluorophenyl)methanimine (1j)

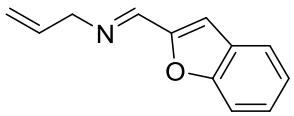
colorless oil. IR: (neat) 3078, 2824, 1650, 1586, 1450 cm^{-1}; ^1H NMR (400 MHz, d-$CDCl_3$) δ 8.60 (s, 1H), 8.00 (td, *J* = 7.6, 2.0 Hz, 1H), 7.36-7.42 (m, 1H), 7.17 (t, *J* =

7.6 Hz, 1H), 7.07 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.02-6.11 (m, 1H), 5.23 (dd, *J* = 17.2, 2.0 Hz, 1H), 5.16 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.28 (dd, *J* = 6.4, 1.6 Hz, 2H). ^{13}C NMR (100 MHz, d-$CDCl_3$) δ 162.5 (d, *J* = 250.9 Hz), 155.5 (d, *J* = 4.8 Hz), 135.9, 132.4 (d, *J* = 8.6 Hz), 127.9 (d, *J* = 2.9 Hz), 124.5 (d, *J* = 1.5 Hz), 124.0, 116.3 (d, *J* = 44.2 Hz), 115.9, 64.1. HRMS (ESI+) calcd. for C10H10FN [M+H] 164.0797, found 164.0799.



(*E*)-*N*-allyl-1-(benzo[b]thiophen-2-yl)methanimine (1n)

White solid, mp = 66-67 ^{o}C. IR: (neat) 2865, 2816, 1630, 1432 cm^{-1}; ^{1}H NMR (300 MHz, d-$CDCl_3$) δ 8.51 (s, 1H), 7.80-7.88 (m, 2H), 7.56 (s, 1H), 7.36-7.44 (m, 2H), 6.04-6.17 (m, 1H), 5.25-5.32 (m, 1H), 5.20-5.24 (m, 1H), 4.32 (dd, *J* = 5.7, 1.5 Hz, 2H). ^{13}C NMR (75 MHz, d-$CDCl_3$) δ 156.1, 142.9, 140.8, 139.5, 135.6, 128.0, 126.3, 124.8, 124.7, 123.0, 116.7, 63.3.



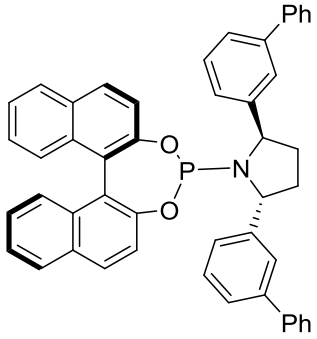
(*E*)-*N*-allyl-1-(benzofuran-2-yl)methanimine (1o)

colorless oil. IR: (neat) 3084, 2884, 2821, 1648, 1450 cm^{-1}; ^{1}H NMR (400 MHz, d-$CDCl_3$) δ 8.26 (s, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.27 (dd, *J* = 8.0, 6.4 Hz, 1H), 7.07 (s, 1H), 6.06-6.16 (m, 1H), 5.27 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.20 (dd, *J* = 10.0, 1.6 Hz, 1H), 4.32 (dd, *J* = 6.0, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, d-$CDCl_3$) δ 155.8, 152.8, 151.2, 135.4, 127.9, 126.7, 123.6, 122.2, 117.1, 112.3, 111.3, 64.1. HRMS (ESI+) calcd. for C12H11NO [M+Na] 208.0738, found 208.0733.

Glycinate nucleophiles: Glycinate benzophenone imines were prepared according to reported literatures.[2]

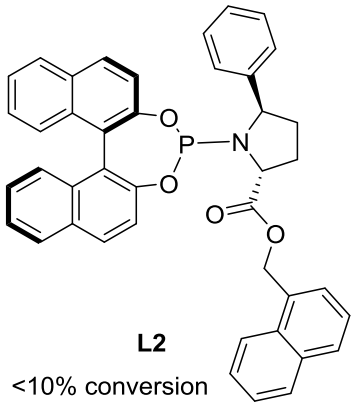
III. Reaction optimization:

No desired product was observed with phosphoramidite ligands or phosphine ligands in our initial studies as shown in **Figure 1**.



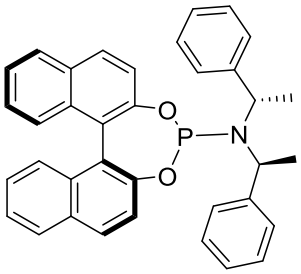
L1

<10% conversion



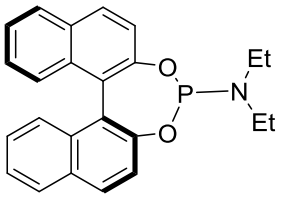
L2

<10% conversion



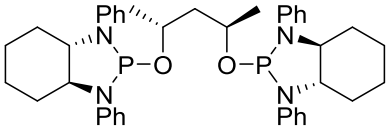
L3

<10% conversion



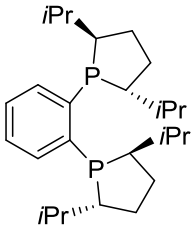
L4

<10% conversion



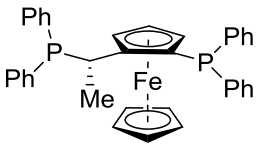
L5

<10% conversion



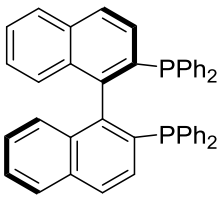
L6

nr



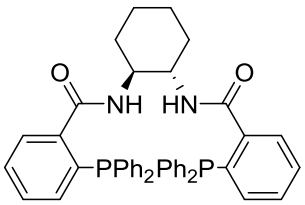
L7

nr



L8

nr



L9

nr

nr = no reaction

Figure 1. Initial ligands screening

We were also interested in improving enantioselectivity by varying glycinate nucleophiles. With DIOP as the standard ligand, a number of glycinates were screened (**Figure 2**). In fact, the two halves of the glycinate structure is of paramount importance. Changing from *N*-dibenzylidene glycinate (**2a**) to *N*-benzylidene glycinate (**2e**) resulted in the decrease of enantioselectivity indicating the importance of bulky aromatic imine substitution for maintaining high level of enantio-induction. Moreover,

fine tuning of the ester moiety of glycinates found that the presence of sterically less demanding substituents were beneficial for enantioselectivity. The highest enantioselectivity (85:15 er) was obtained upon using methyl glycinate (**2b**) as the nucleophile. Surprisingly, replacing methyl ester with cyano group (**2b** vs **2g**) resulted in lower enantioselectivity and poor diastereoselectivity. Further study showed that sterically more demanding substituents on imines, such as 3,5-dimethylphenyl or 2-naphthyl groups, did not have significant impact on the enantioselectivity (**2h** and **2i** vs **2b**).

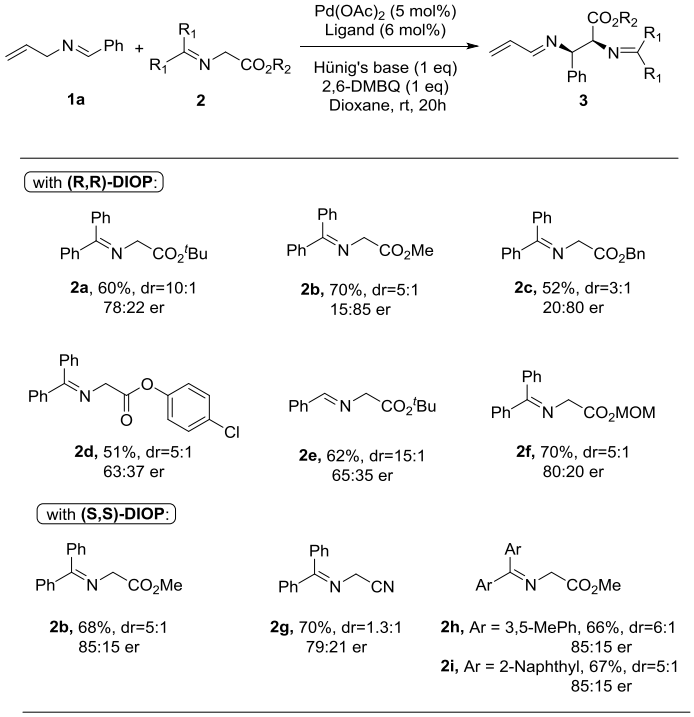
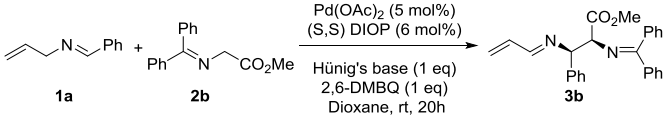


Figure 2. Screening of the glycinates

Efforts to improve the enantioselectivity then shifted to examine the solvent effect (**Table 1**) with dioxane being the standard (**Table 1,** entry 1). Shifting to THF and DME, similar ethereal solvents, showed some differences (entries 2 and 3). Notably, DME improved the diastereoselectivity while maintaining yield and enantioselectivity. When the medium was changed to DCM, however, a complex mixture was observed (entry 4). Aromatic solvents turned out to be generally beneficial for this transformation. A slightly higher enantioselectivity was obtained with toluene as the solvent (entry 6, 87:13 er). Importantly, full conversion was maintained. Although xylene and mesitylene were better solvents in terms of enantioselectivity, reaction conversions were typically poor even after a prolonged reaction time (entry 8 and 9). In an attempt to increase the reaction conversion, a combination of toluene and mesitylene (1:1 mixture) was also examined (entry 10). Although similar enantiomeric excess of the product was obtained, no beneficial effect on either the reaction conversion or the diastereoselectivity was observed.

Table 1. Solvent screening[a]

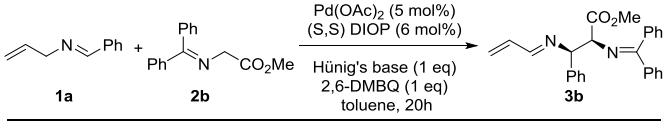


Entry	Solvent	Conversion[c]	Yield[b]	dr[c]	er[d]
1	Dioxane	100%	70%	5:1	85:15
2	THF	100%	65%	4:1	85:15
3	DME	100%	68%	6:1	84:16
4	DCM	100%	messy	-	-
5	Benzene	100%	62%	4:1	85:15
6	Toluene	100%	67%	5:1	87:13
7	2-ClPh	100%	61%	4:1	86:14
8[e]	Xylene	52%	35%	5:1	88:12
9[e]	Mes	47%	38%	5:1	90:10
10[e]	Tol/Mes (1:1)	51%	33%	4:1	86:14

[a]Reaction conditions: **1a** (0.1 mmol), **2b** (0.1 mmol), Pd(OAc)2 (5 mol%), Ligand (6 mol%), Hunig's base (0.1 mmol), 2,6-DMBQ (0.1 mmol), dioxane, rt, 15-20h. [b]Isolated yield. [c]Determined by ^{1}H-NMR. [d]Determined by chiral HPLC. [e]40h.

With toluene as the most effective solvent for this reaction, other reaction parameters, such as temperature and concentration, were further examined (**Table 2**). The reaction was sensitive to temperature. Lowering the temperature from room temperature to 4°C, higher diastereoselectivity and enantioselectivity was observed (entry 2), at the expense of conversion. Increasing the concentration to 0.5 M provided 3b in 49% conversion (entry 3). At 0.8 M and 1.0 M, the reaction also proceeded to 50% conversion, although the isolated yield decreased (entry 4 and 5). Notably in those cases, the enantiomeric excess of the product was maintained (90:10 er). Although this seemed a promising line of inquiry, prolonging the reaction time while maintaining this relatively high reaction concentration of 0.8 M did not significantly improve the isolated yield of **3b** but the diastereoselectivity decreased (entry 6). The asymmetric allylic alkylation proceeded with almost complete conversion after 70h, and afforded **3b** in 58% yield and 89:11 er (entry 7).

Table 2. Temperature and concentration optimization[a]



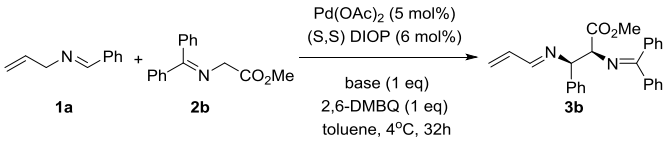
Entry	Tempt &concen	Conver[c]	Yield[b]	dr[c]	er[d]
1	rt, 0.3M	100%	67%	5:1	87:13

2	4°C, 0.3M	32%	25%	9:1	90:10
3	4°C, 0.5M	49%	40%	8:1	90:10
4	4°C, 0.8M	50%	36%	8:1	89:11
5	4°C, 1.0M	52%	32%	8:1	89:11
6[e]	4°C, 0.8M	88%	54%	5:1	89:11
7[e]	4°C, 0.5M	95%	58%	5:1	89:11

[a]Reaction conditions: **1a** (0.1 mmol), **2b** (0.1 mmol), Pd(OAc)2 (5 mol%), Ligand (6 mol%), Hunig's base (0.1 mmol), 2,6-DMBQ (0.1 mmol), dioxane, rt, 15-20h. [b]Isolated yield. [c]Determined by [1]H-NMR. [d]Determined by chiral HPLC. [e]70h.

We examined this transformation with a variety of secondary and tertiary amines (**Table 3**). Triethylamine (entry 2) were remarkably more effective than N,N-diisopropylethyl amine (entry 1) giving the desired product in 65% yield and 90:10 er with full conversion. When N-methylpyrolidine (entry 3), an amine that, with two conformationally-restricted substituents, has less steric bulk than either triethylamine or *N*,*N*-diisopropylethylamine was employed, **3b** was obtained in 85% conversion and 87:13 er. A collection of secondary amines were also examined. With diisopropylamine, the reaction progressed to 80% and produced **3b** in 51% yield (NMR, entry 4). No conversion was observed with morpholine as the base (entry 5). When pyridine was employed, low conversion was obtained (entry 6). No desired product was observed when either DBU (entry 7) or inorganic base, K_2CO_3 (entry 8), were tested. These results suggest the steric demands, rather than the electronics or basicity of the amine, are crucial to both catalyst turnover and enantioinduction.

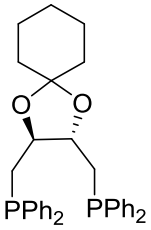
Table 3. Bases screening[a]



Entry	Base	Conversion[c]	Yield[b]	dr[c]	er[d]
1	*i*Pr$_2$NEt	70%	45%	5:1	90:10
2	Et$_3$N	100%	65%	6:1	90:10
3	*N*-Me Pyrolidine	85%	55%	3:1	87:13
4	*i*Pr2NH	80%	51%	5:1	90:10
5	Morpholine	trace	-	-	-
6	Pyridine	30%	19%	5:1	89:11
7	DBU	100%	trace	-	-
8	K_2CO_3	61%	trace	-	-

[a]Reaction conditions: **1a** (0.1 mmol), **2b** (0.1 mmol), Pd(OAc)2 (5 mol%), Ligand (6 mol%), Hunig's base (0.1 mmol), 2,6-DMBQ (0.1 mmol), dioxane, rt, 15-20h. [b]Isolated yield. [c]Determined by ^{1}H-NMR. [d]Determined by chiral HPLC.

DIOP ligands: DIOP ligands were prepared according to established procedures.[3]

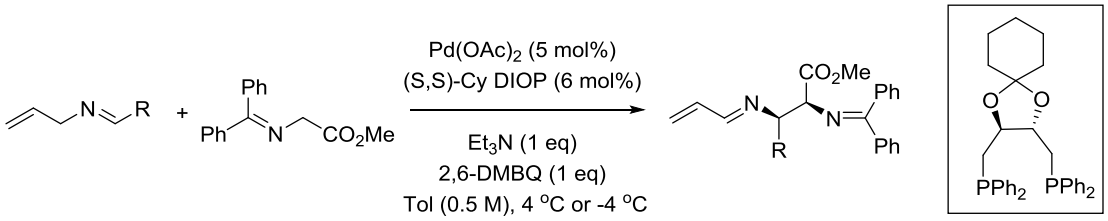


(S,S)-Cy DIOP

(2S,3S)-2,3-bis((diphenylphosphaneyl)methyl)-1,4-dioxaspiro[4.5]decane[3c]

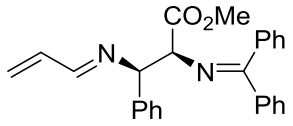
White solid, mp = 86-88 °C. α_D^{25} = +25.2 (*c* = 2.0, $CHCl_3$). ^{1}H NMR (500 MHz, d-$CDCl_3$) δ 7.43-7.48 (m, 8H), 7.33-7.36 (m, 12H), 3.98-4.01 (m, 2H), 2.37-2.46 (m, 4H), 1.57-1.60 (m, 4H), 1.44-1.54 (m, 4H), 1.33 (q, *J* = 6.0 Hz, 2H). ^{13}C NMR (125 MHz, d-$CDCl_3$) δ 138.8 (dd, *J* =15.6, 12.5 Hz), 133.0 (dd, *J* =19.1, 8.3 Hz),128.5-128.8 (m), 109.6, 79.5 (dd, *J* =14.8, 8.0 Hz), 37.0, 32.6, 32.5, 25.3, 24.0. ^{31}P NMR (161 MHz, d-$CDCl_3$) δ -21.6 ppm.

IV. General method for asymmetric allylic alkylations:



General procedure for the Pd-catalyzed asymmetric allylic alkylation involving π-allyl intermediate: An oven dried Pyrex microwave vial was charged with $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and was sealed with a rubber septa. The vial was evacuated and filled with nitrogen three times in an interval of 10 min. In a separate sealed nitrogen flushed vial, glycinate (0.5 mmol) and *N*-allyl imine (0.5 mmol) were taken in freshly distilled toluene (1 ml). The solution was cannulated to the microwave vial with

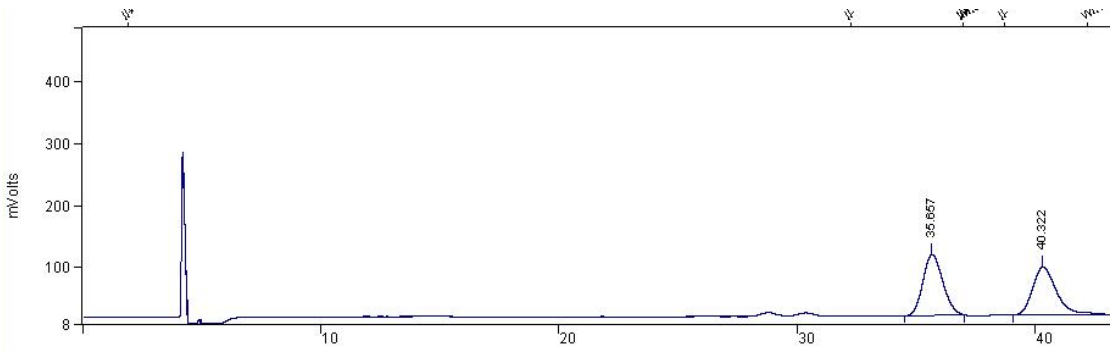
palladium catalyst. Et_3N (50 mg, 0.5 mmol) was added to the resulting turbid solution and was allowed to stir at 4 ^oC or -4 ^oC for 35-60h. Upon completion (monitored by crude NMR), solvent was removed in vacuo and the residue was purified by flash chromatography over silica gel (pre-neutralized with 3% Et_3N in Hexanes), eluting with EtOAc / hexanes/ Et_3N, to give the product.



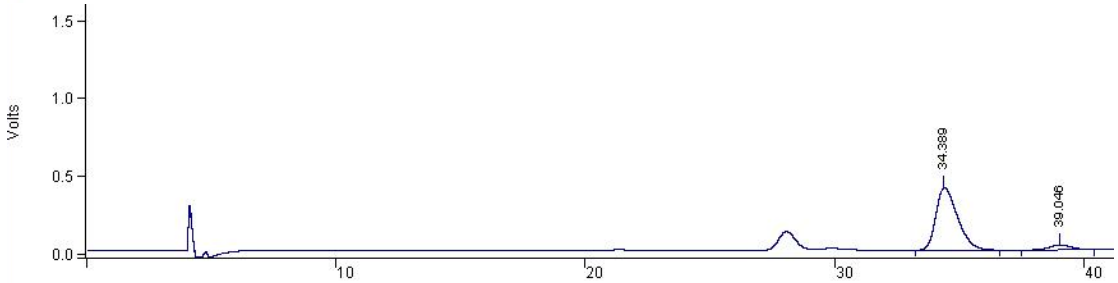
Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-phenyl propanoate (3b)

The reaction was performed with *N*-allyl imine (72.5 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 36 h at 4^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (129 mg, 65%) as a colorless oil. α_D^{25} = -33.7 (*c* = 1.0, $CHCl_3$). IR: (neat) 3017, 2936, 1708, 1622, 1599, 1348 cm^{-1}; ^1H NMR (500 MHz, d-$CDCl_3$) δ 8.06 (d, *J* = 9.0 Hz, 1H), 7.61 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.45-7.47 (m, 3H), 7.39-7.42 (m, 1H), 7.32-7.35 (m, 4H), 7.27-7.29 (m, 2H), 7.23-7.25 (m, 1H), 7.08-7.10 (m, 2H), 6.51-6.58 (m, 1H), 5.73 (d, *J* = 10.5 Hz, 1H), 5.67 (d, *J* = 17.5 Hz, 1H), 4.91 (d, *J* = 8.0 Hz, 1H), 4.58 (d, *J* = 8.0 Hz, 1H), 3.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 170.9, 164.7, 140.2, 139.8, 137.1, 136.5, 130.6, 129.1, 128.9, 128.6, 128.5, 128.3, 128.3, 128.2, 127.9, 127.8, 78.0, 72.0, 52.2. HRMS (ESI+) calcd. for C26H24N2O2 [M+Na] 419.1736, found 419.1723.

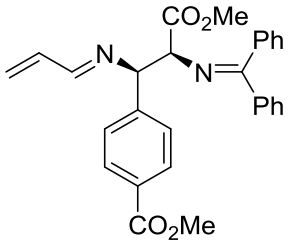
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 100/1/0.1, 254 nm absorbance). Major enantiomer (tR = 34.4 min), minor enantiomer (tR = 39.0 min): er = 92:8.



Peak No.	Peak Name	Result ()	Time (min)	Offset (min)	Area (counts)	Sep. Code	1/2 (sec)	Status Codes
1		50.9229	35.657	0.000	5781827	BB	57.6	
2		49.0771	40.322	0.000	5572260	BB	64.9	U
	Totals:	100.0000		0.000	11354087			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		92.3541	34.389	0.000	24354736	BB	61.3	
2		7.6459	39.046	0.000	2016306	BB	61.4	
	Totals:	100.0000		0.000	26371042			

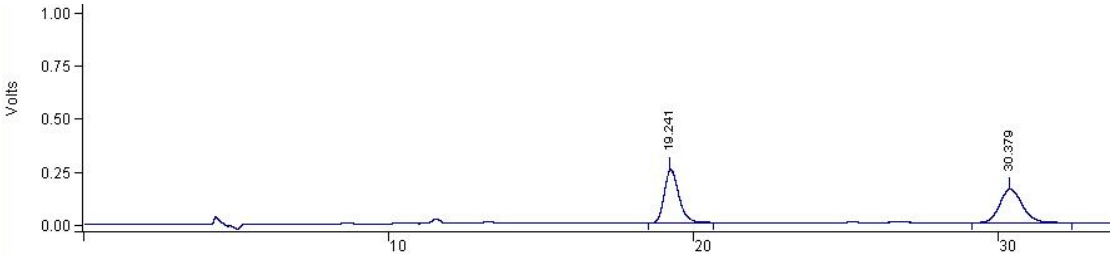


Methyl 4-((1R,2S)-1-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-methoxy-3-oxopropyl)benzoate (3c)

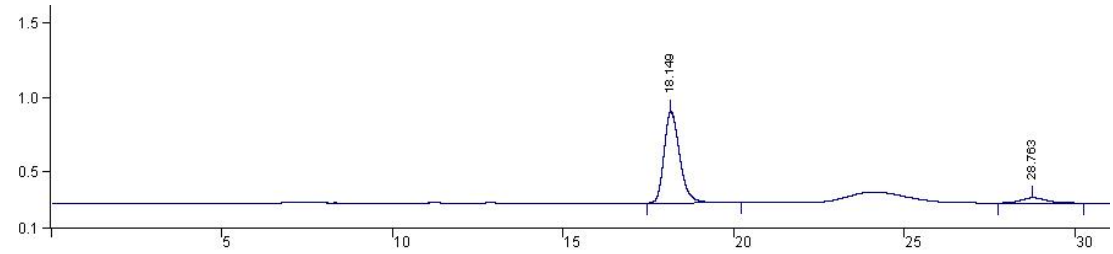
The reaction was performed with *N*-allyl imine (101.6 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 40 h at -4^{o}C. After removing the solvent, purification by flash

chromatography (EtOAC / hexanes /Et_3N = 10/90/1) gave product (170 mg, 75%) as a colorless oil. α_D^{25} = -85.7 (*c* = 1.0, $CHCl_3$). IR: (neat) 3058, 2951, 1723, 1611, 1435 cm^{-1}; ^1H NMR (500 MHz, d-$CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.42-7.44 (m, 3H), 7.36-7.40 (m, 3H), 7.29-7.32 (m, 2H), 7.03-7.05 (m, 2H), 6.48-6.56 (m, 1H), 5.73 (d, *J* = 10.5 Hz, 1H), 5.66 (d, *J* = 17.5 Hz, 1H), 4.93 (d, *J* = 7.5 Hz, 1H), 4.53 (d, *J* = 7.5 Hz, 1H), 3.87 (s, 3H), 3.51 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 170.6, 167.1, 165.2, 145.4, 139.6, 137.0, 136.3, 130.7, 129.8, 129.5, 129.1, 128.9, 128.6, 128.3, 128.2, 128.1, 128.1, 77.5, 71.2, 52.3. HRMS (ESI+) calcd. for C28H26N2O4 [M+Na] 477.1790, found 477.1771.

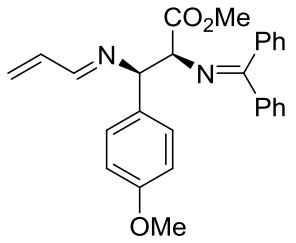
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 20/1/0.1, 254 nm absorbance). Major enantiomer (tR = 18.1 min), minor enantiomer (tR = 28.7 min): er = 92:8.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.8642	19.241	0.000	8371189	BB	30.8	
2		49.1358	30.379	0.000	8086733	BB	47.5	
	Totals:	100.0000		0.000	16457922			



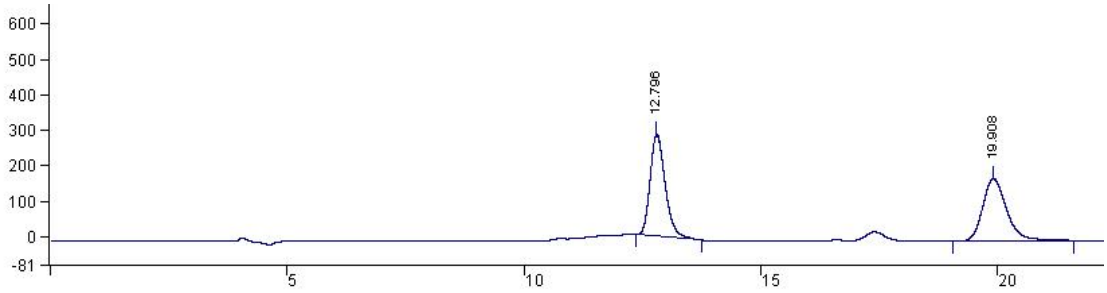
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		92.0109	18.149	0.000	19624650	BB	29.3	
2		7.9891	28.763	0.000	1703957	BB	45.3	
	Totals:	100.0000		0.000	21328607			



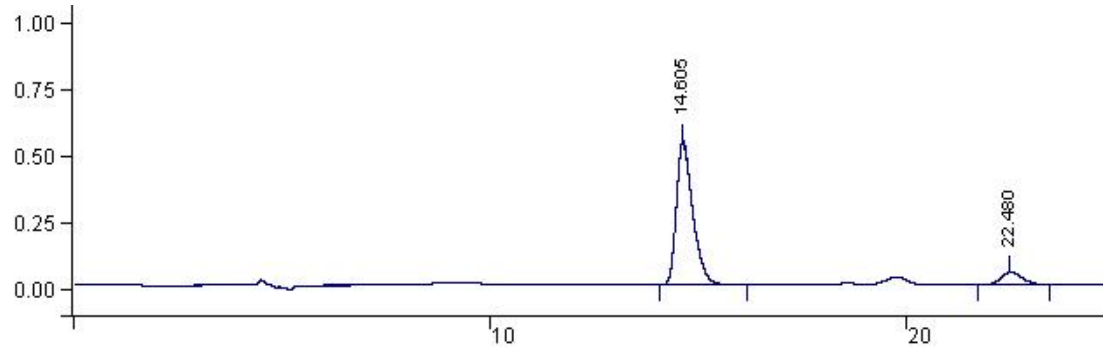
Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-(4-methoxyphenyl)propanoate (3d)

The reaction was performed with *N*-allyl imine (87.6 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 40 h at 4^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (149 mg, 70%) as a colorless oil. α_D^{25} = -51.6 (*c* = 2.0, $CHCl_3$). IR: (neat) 3059, 2950, 1741, 1611, 1511 cm^{-1}; ^1H NMR (500 MHz, d-$CDCl_3$) δ 7.98 (d, *J* = 9.0 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.41-7.43 (m, 3H), 7.34-7.37 (m, 1H), 7.28-7.32 (m, 2H), 7.20 (d, *J* = 9.0 Hz, 2H), 7.06-7.08 (m, 2H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.43-6.50 (m, 1H), 5.67 (d, *J* = 10.0 Hz, 1H), 5.62 (d, *J* = 17.0 Hz, 1H), 4.80 (d, *J* = 8.0 Hz, 1H), 4.50 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 3H), 3.50 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 171.0, 164.4, 159.1, 139.9, 137.2, 136.5, 132.3, 130.6, 129.3, 129.1, 128.9, 128.6, 128.3, 128.2, 127.8, 113.9, 77.4, 72.1, 55.4, 52.2. HRMS (ESI+) calcd. for C27H26N2O3 [M+Na] 449.1841, found 449.1834.

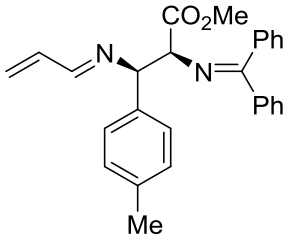
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 20/1/0.1, 254 nm absorbance). Major enantiomer (tR = 14.6 min), minor enantiomer (tR = 22.5 min): er = 89.5 :10.5.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.6349	12.796	0.000	6383686	BB	19.7	
2		49.3651	19.908	0.000	6223598	BB	31.5	
	Totals:	100.0000		0.000	12607284			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		89.4952	14.605	0.000	14988652	BB	24.9	
2		10.5048	22.480	0.000	1759343	BB	33.8	
	Totals:	100.0000		0.000	16747995			

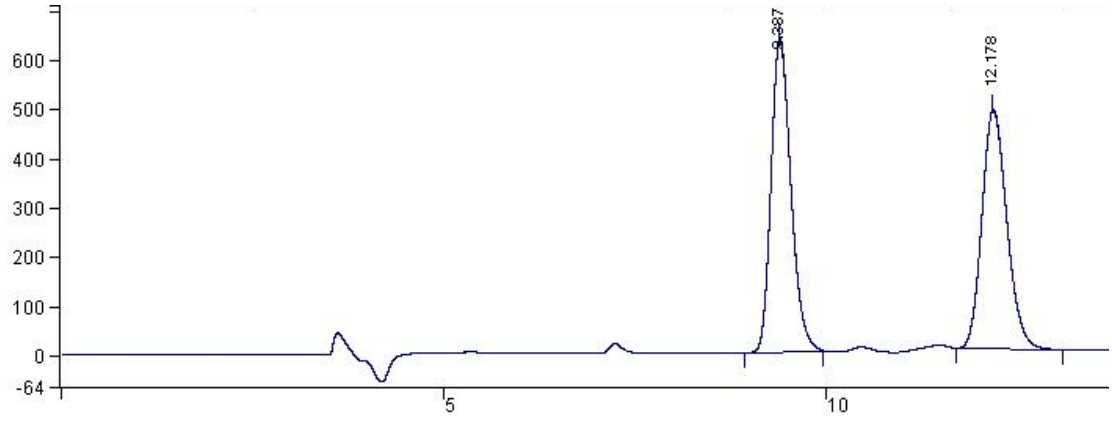


Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-(4-methylphenyl)propanoate (3e)

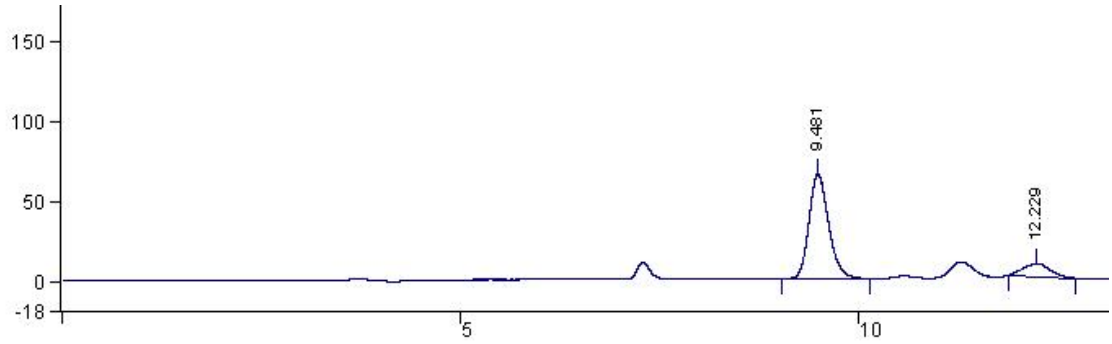
The reaction was performed with *N*-allyl imine (87.6 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in

toluene (1.0 mL) for 40 h at 4°C. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (127 mg, 62%) as a colorless oil. α_D^{25} = -55.2 (*c* = 1.0, $CHCl_3$). IR: (neat) 3056, 3026, 1742, 1645, 1621, 1446 cm^{-1}; ^1H NMR (400 MHz, d-$CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.42-7.44 (m, 3H), 7.35-7.38 (m, 1H), 7.28-7.33 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.04-7.10 (m, 4H), 6.45-6.54 (m, 1H), 5.68 (d, *J* = 10.0 Hz, 1H), 5.63 (d, *J* = 17.2 Hz, 1H), 4.84 (d, *J* = 8.0 Hz, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 3.52 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 171.0, 164.5, 139.9, 137.3, 137.2, 137.1, 136.5, 130.5, 129.2, 129.1, 128.8, 128.5, 128.3, 128.1, 128.1, 127.8, 77.7, 72.1, 52.1, 21.3. HRMS (ESI+) calcd. for C27H26N2O2 [M+Na] 433.1881, found 433.1886.

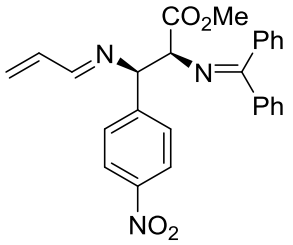
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 20/1/0.1, 254 nm absorbance). Major enantiomer (tR = 9.5 min), minor enantiomer (tR = 12.2 min): er = 86 :14.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.9612	9.387	0.000	11516488	BB	16.5	
2		49.0388	12.178	0.000	11082073	BB	20.8	
	Totals:	100.0000		0.000	22598561			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		86.3748	9.481	0.000	1127036	BB	15.5	
2		13.6252	12.229	0.000	177784	BB	20.6	
	Totals:	100.0000		0.000	1304820			

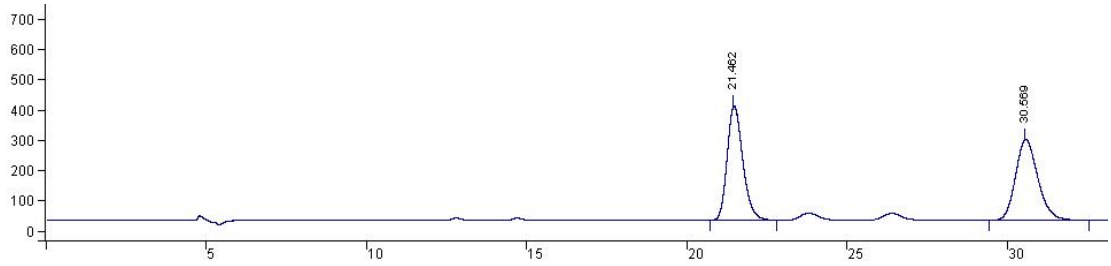


Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-(4-nitrophenyl)propanoate (3f)

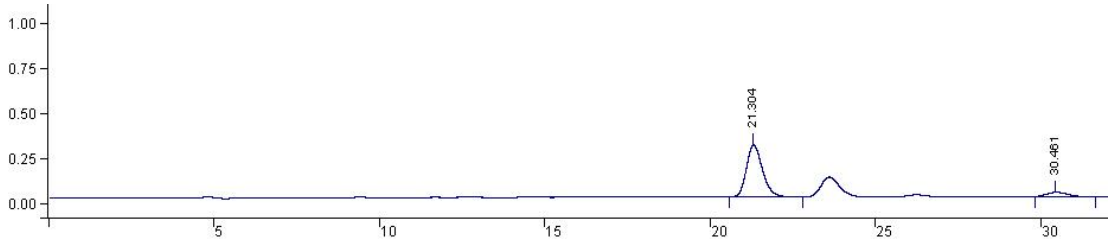
The reaction was performed with *N*-allyl imine (95.1 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 72 h at -20^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (154 mg, 70%) as a colorless oil. α_D^{25} = -77.1 (*c* = 1.0, $CHCl_3$). IR: (neat) 3057, 1741, 1646, 1599, 1521 cm^{-1}; ^1H NMR (500 MHz, d-$CDCl_3$) major diastereomer: δ 8.10 (d, *J* = 9.0 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.54 (d, *J* = 9.0 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 2H), 7.42-7.43 (m, 3H), 7.34-7.37 (m, 1H), 7.27-7.30 (m, 2H), 7.04-7.06 (m, 2H), 6.44-6.52 (m, 1H), 5.72 (d, *J* = 10.0 Hz, 1H), 5.66 (d, *J* = 17.0 Hz, 1H), 4.91 (d, *J* = 8.0 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 1H), 3.54 (s, 3H). minor diastereomer: δ 8.08 (d, *J* = 9.0 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.68 (d, *J* = 9.0 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.42-7.47 (m, 3H), 7.36-7.37 (m, 1H), 7.27-7.30 (m, 2H), 7.04-7.06 (m, 2H), 6.42-6.47 (m, 1H), 5.83 (d, *J*

= 10.0 Hz, 1H), 5.75 (d, *J* = 17.0 Hz, 1H), 5.03 (d, *J* = 8.5 Hz, 1H), 4.63 (d, *J* = 8.5 Hz, 1H), 3.70 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 170.4, 165.6, 147.8, 147.5, 139.4, 136.8, 136.2, 130.9, 129.3, 129.1, 128.9, 128.7, 128.3, 128.2, 128.1, 123.7, 77.0, 71.6, 52.4. HRMS (ESI+) calcd. for C26H23N3O4 [M+Na] 464.1586, found 464.1578.

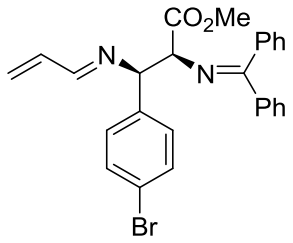
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 20/1/0.1, 254 nm absorbance). Major enantiomer (tR = 21.3 min), minor enantiomer (tR = 30.5 min): er = 90 :10.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.0223	21.462	0.000	12900804	BB	31.8	
2		49.9777	30.569	0.000	12889284	BB	44.5	
	Totals:	100.0000		0.000	25790088			



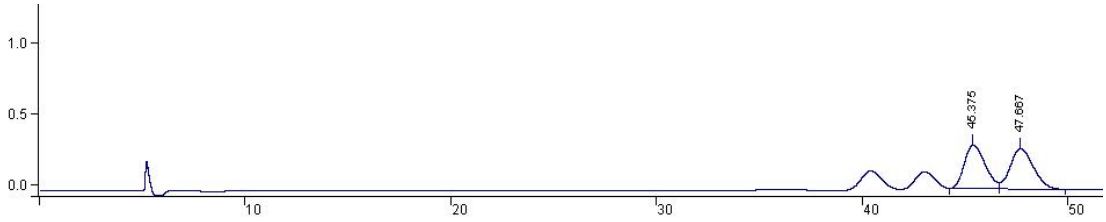
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		90.3347	21.304	0.000	9881343	BB	31.8	
2		9.6653	30.461	0.000	1057248	BB	40.6	
	Totals:	100.0000		0.000	10938591			



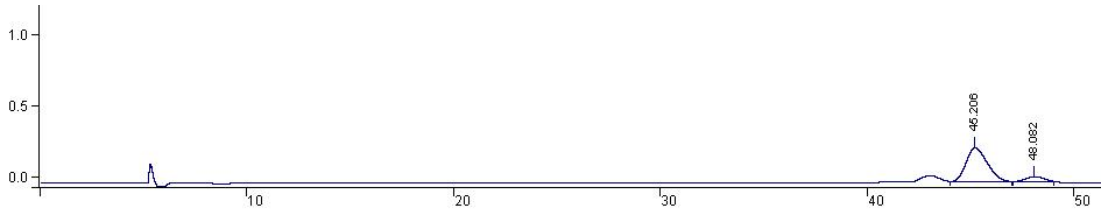
Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-(4-bromophenyl)propanoate (3g)

The reaction was performed with *N*-allyl imine (111.0 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 42 h at -4 ^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (200 mg, 84%) as a colorless oil. α_D^{25} = -102 (*c* = 3.0, $CHCl_3$). IR: (neat) 3057, 2950, 1742, 1621, 1487, 1446 cm^{-1}; ^1H NMR (500 MHz, d-$CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 2H), 7.43-7.47 (m, 4H), 7.36-7.38 (m, 1H), 7.29-7.34 (m, 3H), 7.24-7.25 (m, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.02-7.05 (m, 2H), 6.48-6.55 (m, 1H), 5.73 (d, *J* = 10.0 Hz, 1H), 5.66 (d, *J* = 17.0 Hz, 1H), 4.85 (d, *J* = 8.0 Hz, 1H), 4.51 (d, *J* = 8.0 Hz, 1H), 3.56 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 170.7, 165.2, 142.6, 139.6, 137.0, 136.3, 131.6, 131.3, 130.8, 130.0, 129.1, 129.0, 128.6, 128.1, 126.9, 122.5, 77.1, 71.7, 52.3. HRMS (ESI+) calcd. for C26H23BrN2O2 [M+H] 475.1013, found 475.1016.

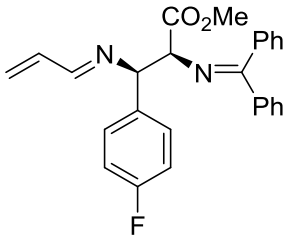
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 150/1/0.1, 254 nm absorbance). Major enantiomer (tR = 45.2 min), minor enantiomer (tR = 48.0 min): er = 90 :10.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		49.1020	45.375	0.000	21620838	BV	72.0	
2		50.8980	47.667	0.000	22411654	VB	76.7	
	Totals:	100.0000		0.000	44032492			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		90.1788	45.206	0.000	16814282	BB	73.1	
2		9.8212	48.082	0.000	1831211	BB	62.0	
	Totals:	100.0000		0.000	18645493			

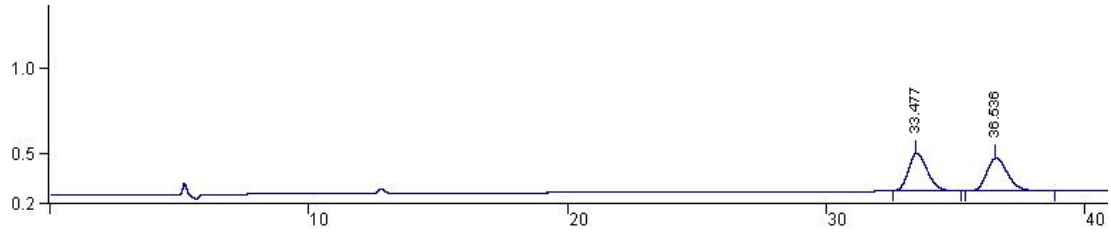


Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-(4-fluorophenyl)propanoate (3h)

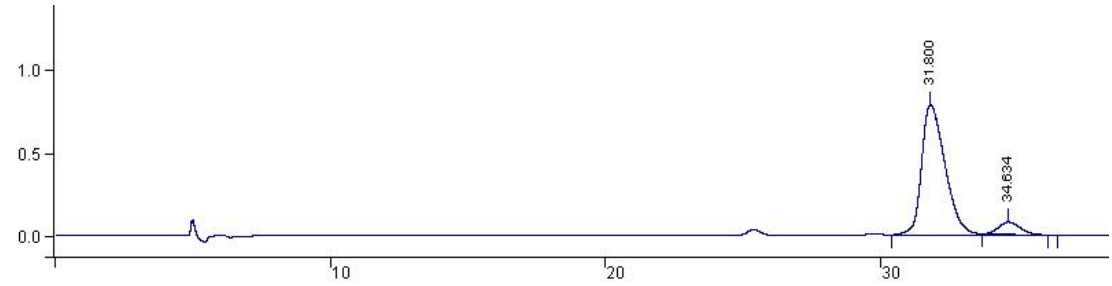
The reaction was performed with *N*-allyl imine (81.6 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 42 h at -4^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (149 mg, 72%) as a colorless oil. α_D^{25} = -62.4 (*c* = 1.0, $CHCl_3$). IR: (neat) 3058, 1742, 1604, 1508 cm^{-1}; ^1H NMR (500 MHz, d-$CDCl_3$) δ 8.01 (d, *J* = 9.0 Hz, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.43-7.45 (m, 3H), 7.35-7.38 (m, 1H), 7.28-7.32 (m, 4H), 7.09 (dd, *J* = 7.5, 2.0 Hz, 2H), 6.94 (t, *J* = 8.5 Hz, 2H), 6.43-6.52 (m, 1H), 5.70 (d, *J* = 10.5 Hz, 1H), 5.64 (d, *J* = 17.0 Hz, 1H), 4.82 (d, *J* = 8.0 Hz, 1H), 4.35 (d, *J* = 8.0 Hz, 1H), 3.51 (s, 3H). ^{13}C NMR (125

MHz, $CDCl_3$) δ 172.5, 170.8, 164.8, 162.3 (d, *J* = 244 Hz), 139.7, 137.0, 136.4, 136.0, 130.7, 129.8 (d, *J* = 8.0 Hz), 129.1, 128.8, 128.6, 128.3, 128.1, 127.9, 115.2 (d, *J* = 21.3 Hz), 77.1, 72.0, 52.2. HRMS (ESI+) calcd. for C26H23FN2O2 [M+Na] 437.1641, found 437.1638.

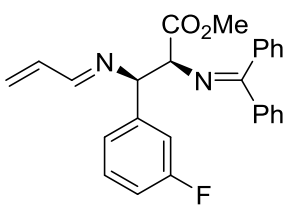
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 100/1/0.1, 254 nm absorbance). Major enantiomer (tR = 31.8 min), minor enantiomer (tR = 34.6 min): er = 92.5 :7.5.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.3642	33.477	0.000	11005453	BB	48.9	
2		49.6358	36.536	0.000	10846293	BB	52.8	
	Totals:	100.0000		0.000	21851746			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		92.4230	31.800	0.000	46796644	BB	60.6	
2		7.5770	34.634	0.000	3836471	TS	0.0	
	Totals:	100.0000		0.000	50633115			

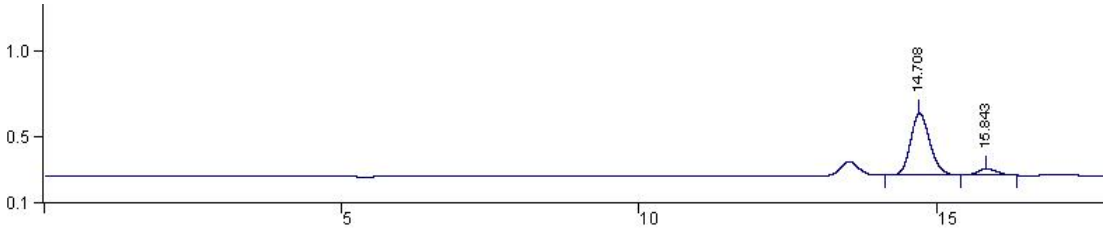


Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-(3-fluorophenyl)propanoate (3i)

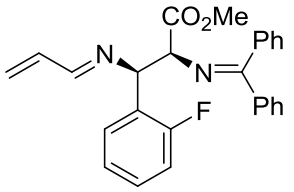
The reaction was performed with *N*-allyl imine (81.6 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 42 h at -4^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (155 mg, 75%) as a colorless oil. α_D^{25} = -52.5 (*c* = 2.0, $CHCl_3$). IR: (neat) 3061, 2952, 1742, 1619, 1446, 1325 cm^{-1}; ^1H NMR (500 MHz, d-$CDCl_3$) δ 8.05 (d, *J* = 9.0 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.46-7.48 (m, 3H), 7.39-7.41 (m, 1H), 7.32-7.35 (m, 2H), 7.22-7.26 (m, 1H), 7.07-7.12 (m, 4H), 6.91-6.94 (m, 1H), 6.50-6.56 (m, 1H), 5.75 (d, *J* = 10.5 Hz, 1H), 5.68 (d, *J* = 17.5 Hz, 1H), 4.89 (d, *J* = 8.0 Hz, 1H), 4.53 (d, *J* = 7.5 Hz, 1H), 3.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 170.7, 165.0, 162.8 (d, *J* = 244 Hz), 142.8, 139.7, 137.0, 136.4, 130.7, 130.0 (d, *J* = 8.0 Hz), 129.1, 128.9, 128.6, 128.3, 128.3, 128.2, 123.9 (d, *J* = 2.5 Hz), 115.3 (d, *J* = 21.8 Hz), 114.7 (d, *J* = 21 Hz), 76.8, 71.8, 52.2. HRMS (ESI+) calcd. for C26H23FN2O2 [M+Na] 437.1641, found 437.1638.

Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 20/1/0.1, 254 nm absorbance). Major enantiomer (tR = 14.7 min), minor enantiomer (tR = 15.8 min): er = 90.5 :9.5.

Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.5930	13.759	0.000	3056821	BV	19.5	
2		49.4070	14.718	0.000	2985165	VB	20.8	
	Totals:	100.0000		0.000	6041986			



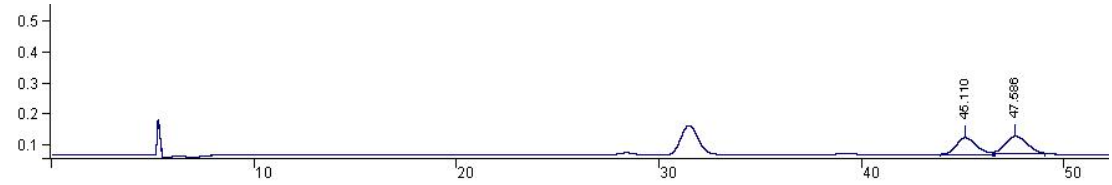
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		90.4709	14.708	0.000	8270483	BV	20.8	
2		9.5291	15.843	0.000	871112	VB	21.6	
	Totals:	100.0000		0.000	9141595			



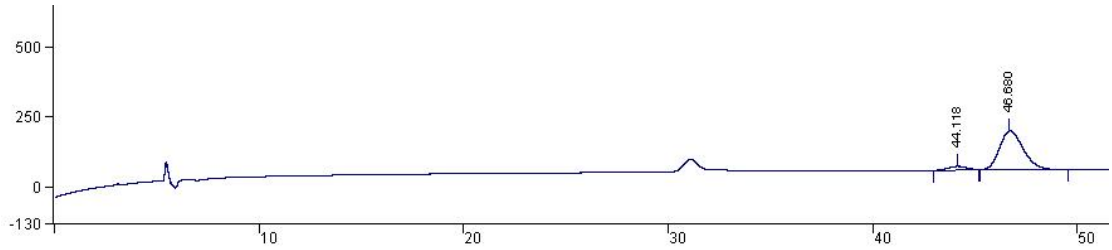
Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-(2-fluorophenyl)propanoate (3j)

The reaction was performed with *N*-allyl imine (81.6 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 42 h at -4^{o}C. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (157 mg, 76%) as a colorless oil. α_D^{25} = -35.3 (*c* = 1.0, $CHCl_3$). IR: (neat) 3059, 2951, 1742, 1644, 1621, 1490 cm^{-1}; ^{1}H NMR (500 MHz, d-$CDCl_3$) δ 8.09 (d, *J* = 9.0 Hz, 1H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.44-7.45 (m, 4H), 7.38-7.41 (m, 1H), 7.31-7.34 (m, 2H), 7.18-7.21 (s, 1H), 7.08 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.03-7.06 (m, 2H), 6.96-7.00 (m, 1H), 6.53-6.60 (m, 1H), 5.76 (d, *J* = 10.5 Hz, 1H), 5.70 (d, *J* = 17.5 Hz, 1H), 5.28 (d, *J* = 7.5 Hz, 1H), 4.68 (d, *J* = 7.0 Hz, 1H), 3.61 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 170.7, 165.7, 160.2 (d, *J* = 244 Hz), 139.7, 137.1, 136.4, 130.6, 130.2 (d, *J* = 2.5 Hz), 129.2, 129.1, 128.9, 128.6, 128.5, 128.3 (d, *J* = 3.3 Hz), 128.1, 127.3 (d, *J* = 13.3 Hz), 124.3, 115.4 (d, *J* = 22.1 Hz), 71.6, 70.0 (d, *J* = 16.3 Hz), 52.3. HRMS (ESI+) calcd. for C26H23FN2O2 [M+Na] 437.1641, found 437.1628.

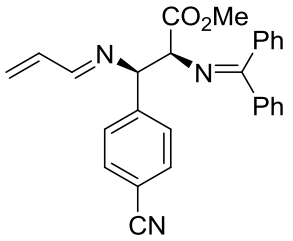
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 100/1/0.1, 254 nm absorbance). Minor enantiomer (tR = 44.1 min), major enantiomer (tR = 46.7 min): er = 7 :93.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		48.0339	45.110	0.000	3687394	BV	66.4	U
2		51.9661	47.586	0.000	3989255	VB	74.6	U
	Totals:	100.0000		0.000	7676649			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		6.6898	44.118	0.000	798494	BB	67.7	
2		93.3102	46.680	0.000	11137474	BB	77.3	
	Totals:	100.0000		0.000	11935968			

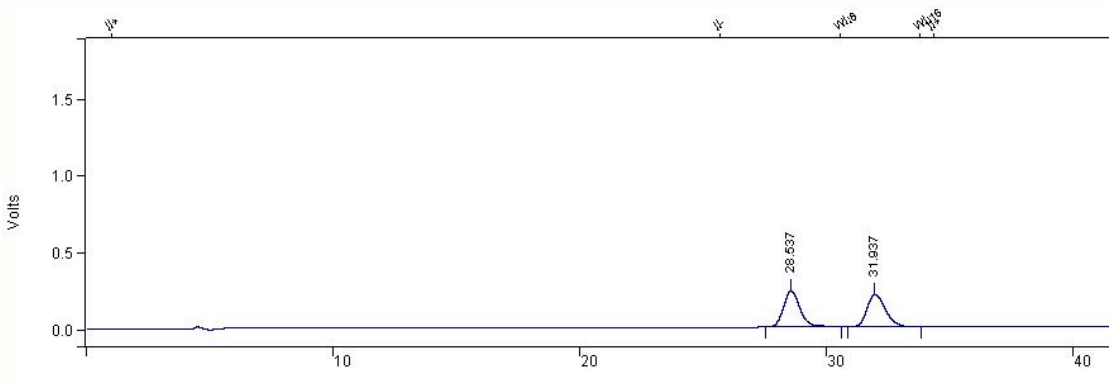


Methyl (2S,3R)-3-(((E)-allylidene)amino)-3-(4-cyanophenyl)-2 -((diphenylmethylene)amino)propanoate (3k)

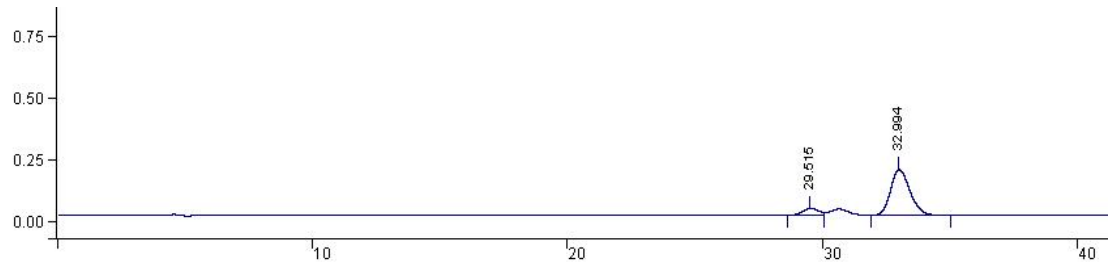
The reaction was performed with *N*-allyl imine (84.1 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in

toluene (1.0 mL) for 40 h at -4 ^{o}C. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (147 mg, 70%) as a colorless oil. α_D^{25} = -77.7 (*c* = 2.0, $CHCl_3$). IR: (neat) 3054, 2228, 1741, 1606, 1576 cm^{-1}; ^{1}H NMR (500 MHz, d-$CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 1H), 7.54-7.57 (m, 4H), 7.43-7.45 (m, 5H), 7.31-7.37 (m, 1H), 7.30-7.33 (m, 2H), 7.03-7.05 (m, 2H), 6.46-6.52 (m, 1H), 5.75 (d, *J* = 10.0 Hz, 1H), 5.67 (d, *J* = 17.0 Hz, 1H), 4.91 (d, *J* = 7.5 Hz, 1H), 4.48 (d, *J* = 7.5 Hz, 1H), 3.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.0, 170.4, 165.5, 145.8, 139.4, 136.8, 136.2, 132.3, 130.8, 129.2, 129.1, 129.1, 128.8, 128.7, 128.2, 128.1, 119.0, 111.5, 77.3, 71.5, 52.4. HRMS (ESI+) calcd. for C27H23N3O2 [M+Na] 444.1670, found 444.1682.

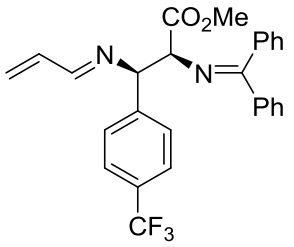
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 20/1/0.1, 254 nm absorbance). Minor enantiomer (tR = 29.5 min), major enantiomer (tR = 33.0 min): er = 11.5 :88.5.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.2198	28.537	0.000	10957139	BB	43.1	
2		49.7801	31.937	0.000	10861204	BB	48.3	
	Totals:	99.9999		0.000	21818343			



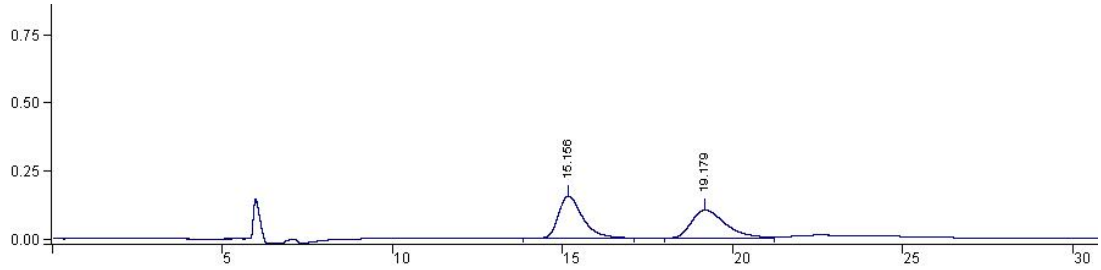
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		11.5250	29.515	0.000	1268972	BB	46.2	
2		88.4750	32.994	0.000	9741600	BB	49.3	
	Totals:	100.0000		0.000	11010572			



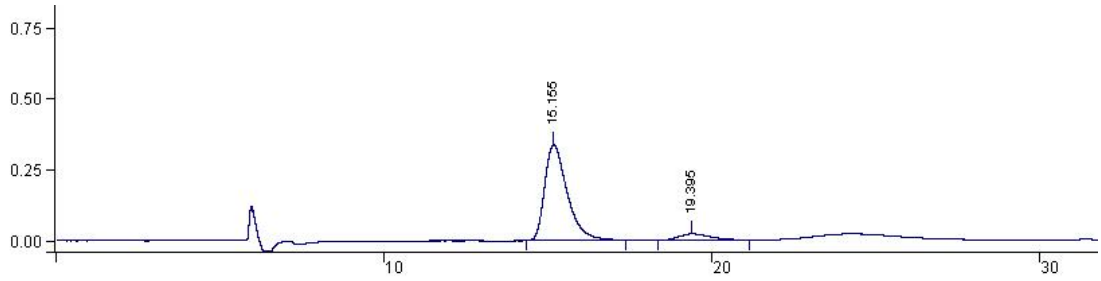
Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-(4-trifluromethylphenyl)propanoate (3l)

The reaction was performed with *N*-allyl imine (106.2 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 72 h at -4^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (167 mg, 72%) as a colorless oil. α_D^{25} = -83.4 (*c* = 1.0, $CHCl_3$). IR: (neat) 3062, 2952, 1743, 1651, 1618, 1326 cm^{-1}; ^1H NMR (500 MHz, d-$CDCl_3$) δ 8.03 (d, *J* = 9.0 Hz, 1H), 7.57-7.59 (m, 2H), 7.49-7.52 (m, 2H), 7.43-7.45 (m, 3H), 7.35-7.38 (m, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.27-7.30 (m, 1H), 7.04-7.06 (m, 2H), 6.47-6.54 (m, 1H), 5.73 (d, *J* = 10.5 Hz, 1H), 5.67 (d, *J* = 17.5 Hz, 1H), 4.93 (d, *J* = 7.5 Hz, 1H), 4.53 (d, *J* = 7.5 Hz, 1H), 3.53 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 170.6, 165.3, 144.4, 139.6, 137.0, 136.9, 136.3, 135.6, 130.8, 129.9 (d, *J* = 32 Hz), 129.1, 128.7, 128.6, 128.2, 128.1 (d, *J* = 5 Hz), 125.4, 124.1 (d, *J* = 267 Hz), 77.3, 71.7, 52.3. HRMS (ESI+) calcd. for C27H23F3N2O2 [M+Na] 487.1593, found 487.1604.

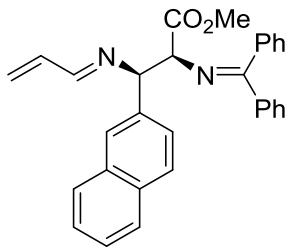
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 0.8 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 100/1/0.1, 254 nm absorbance). Major enantiomer (tR = 15.1 min), minor enantiomer (tR = 19.4 min): er = 91.5 :8.5.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.7857	15.156	0.000	7621719	BB	47.0	
2		49.2143	19.179	0.000	7385892	BB	66.1	
	Totals:	100.0000		0.000	15007611			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		91.4727	15.155	0.000	16156736	BB	46.4	
2		8.5273	19.395	0.000	1506163	BB	66.6	
	Totals:	100.0000		0.000	17662899			

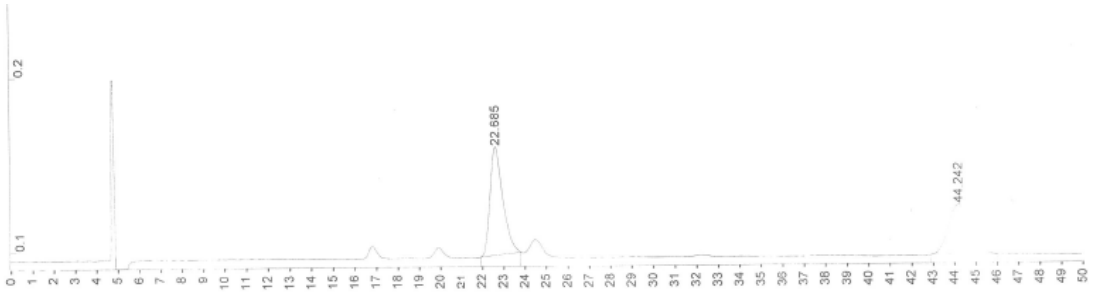


Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-(naphthalene-2-yl)propanoate (3m)

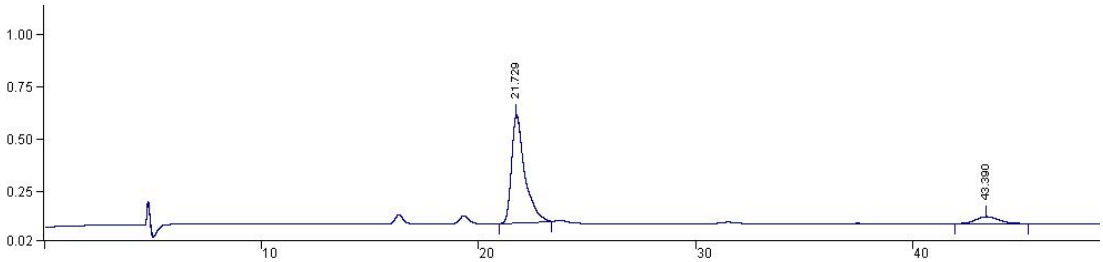
The reaction was performed with *N*-allyl imine (97.6 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 40 h at 4^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (167 mg, 75%) as a

colorless oil. α_D^{25} = -70.5 (*c* = 1.0, $CHCl_3$). IR: (neat) 3057, 2950, 1741, 1621, 1446 cm^{-1}; ^1H NMR (400 MHz, d-$CDCl_3$) δ 8.08 (d, *J* = 9.2 Hz, 1H), 7.75-7.77 (m, 3H), 7.72-7.74 (m, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.40-7.45 (m, 6H), 7.36-7.38 (m, 1H), 7.29-7.33 (m, 2H), 7.04-7.07 (m, 2H), 6.49-6.55 (m, 1H), 5.72 (d, *J* = 10.4 Hz, 1H), 5.66 (d, *J* = 17.2 Hz, 1H), 5.04 (d, *J* = 8.0 Hz, 1H), 4.66 (d, *J* = 8.0 Hz, 1H), 3.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.4, 170.9, 164.9, 139.8, 137.7, 137.1, 136.5, 133.5, 133.1, 131.1, 130.6, 129.2, 128.9, 128.6, 128.3, 128.2, 128.2, 128.1, 127.8, 127.2, 126.3, 126.1, 126.0, 78.1, 71.9, 52.2. HRMS (ESI+) calcd. for C30H26N2O2 [M+Na] 469.1892, found 469.1882.

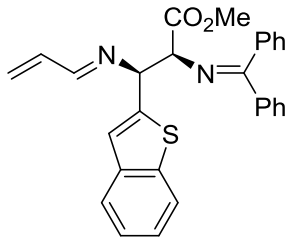
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 40/1/0.1, 254 nm absorbance). Major enantiomer (tR = 21.7 min), minor enantiomer (tR = 43.4 min): er = 90 :10.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.5346	22.685	0.000	2113546	BB	36.6	
2		49.4654	44.242	0.000	2068831	BB	67.9	
	Totals:	100.0000		0.000	4182377			



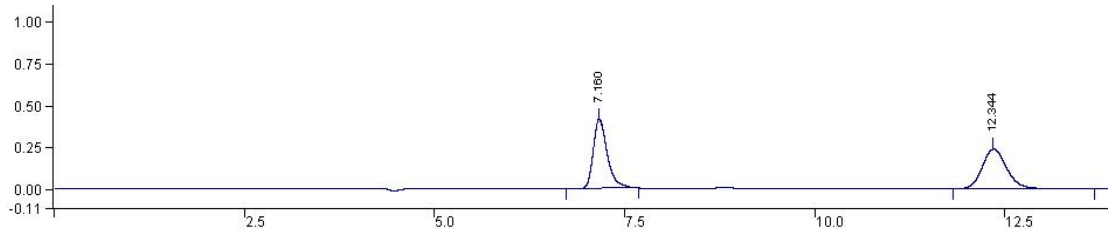
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		90.2635	21.729	0.000	21758568	BB	37.4	
2		9.7365	43.390	0.000	2347048	BB	67.7	
	Totals:	100.0000		0.000	24105616			



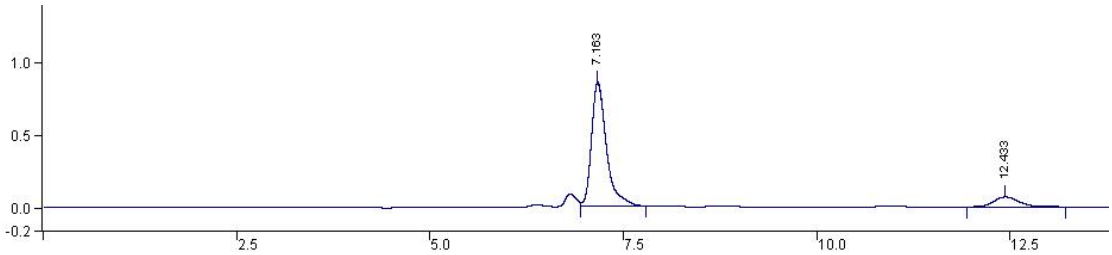
Methyl (2S,3S)-3-(((E)-allylidene)amino)-3-(benzo[b]thiophen-2-yl)-2-((diphenyl methylene)amino)propanoate (3n)

The reaction was performed with *N*-allyl imine (99.8 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 62 h at 4 ^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (138 mg, 61%) as a colorless oil. α_D^{25} = -49.5 (*c* = 1.0, $CHCl_3$). IR: (neat) 3057, 2950, 1741, 1645, 1620 cm^{-1}; ^1H NMR (500 MHz, d-$CDCl_3$) δ 8.10 (d, *J* = 9.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.66-7.68 (m, 2H), 7.47-7.49 (m, 3H), 7.42-7.47 (m, 1H), 7.35-7.38 (m, 2H), 7.28-7.32 (m, 2H), 7.23 (s, 1H), 7.17-7.19 (m, 2H), 6.56-6.62 (m, 1H), 5.78 (d, *J* = 10.5 Hz, 1H), 5.73 (d, *J* = 17.5 Hz, 1H), 5.37 (d, *J* = 7.5 Hz, 1H), 4.68 (d, *J* = 7.5 Hz, 1H), 3.64 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 170.6, 165.4, 143.9, 140.0, 139.6, 139.4, 136.9, 136.2, 130.7, 129.2, 128.9, 128.6, 128.2, 128.1, 124.2, 124.1, 123.5, 122.4, 121.6, 72.9, 71.8, 52.4. HRMS (ESI+) calcd. for C28H24N2O2S [M+Na] 475.1441, found 475.1451.

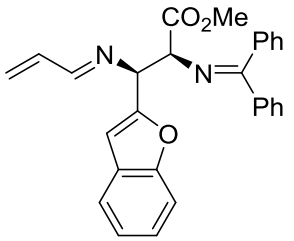
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 20/1/0.1, 254 nm absorbance). Major enantiomer (tR = 7.2 min), minor enantiomer (tR = 12.4 min): er = 88.5 :11.5.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.4046	7.160	0.000	5327029	BB	11.4	
2		49.5954	12.344	0.000	5241515	BB	20.2	
	Totals:	100.0000		0.000	10568544			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		88.4071	7.163	0.000	11505078	BB	11.4	
2		11.5929	12.433	0.000	1508671	BB	20.7	
	Totals:	100.0000		0.000	13013749			

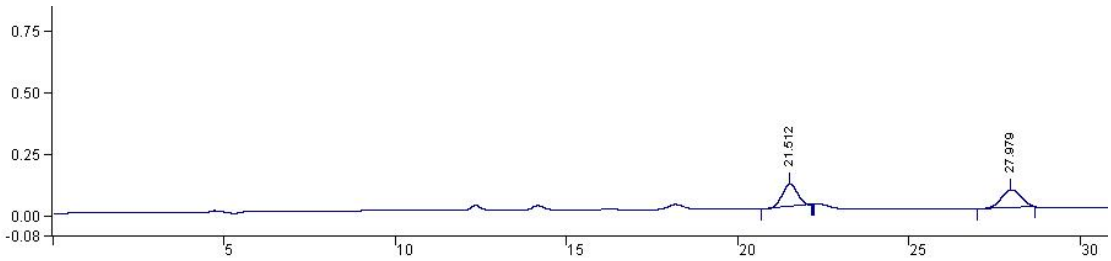


Methyl (2S,3S)-3-(((E)-allylidene)amino)-3-(benzofuran-2-yl)-2 -((diphenylmethylene)amino)propanoate (3o)

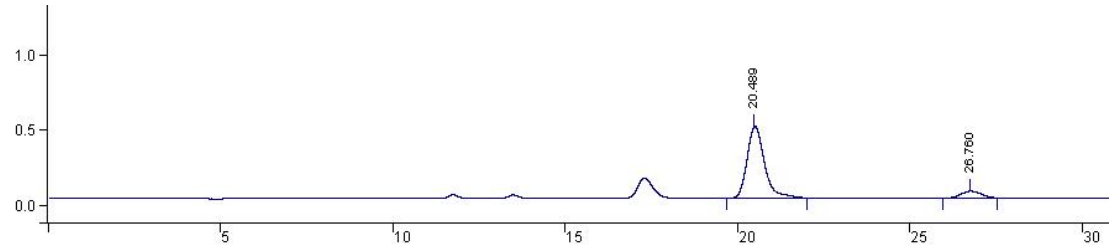
The reaction was performed with *N*-allyl imine (92.6 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 50 h at 4^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (144 mg, 66%) as a

colorless oil. α_D^{25} = -58.2 (*c* = 1.0, $CHCl_3$). IR: (neat) 3058, 1742, 1622, 1454 cm^{-1}; ^1H NMR (500 MHz, d-$CDCl_3$) δ 8.13 (d, *J* = 9.0 Hz, 1H), 7.59-7.61 (m, 2H), 7.49-7.51 (m, 1H), 7.46-7.47 (m, 3H), 7.38-7.42 (m, 2H), 7.31-7.34 (m, 2H), 7.19-7.24 (m, 2H), 7.16-7.18 (m, 2H), 6.62 (s, 1H), 6.55-6.60 (m, 1H), 5.79 (d, *J* = 11.0 Hz, 1H), 5.75(d, *J* = 17.5 Hz, 1H), 5.14 (d, *J* = 8.0 Hz, 1H), 4.66 (d, *J* = 8.0 Hz, 1H), 3.65 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.9, 170.6, 166.7, 155.6, 155.0, 139.8, 136.9, 136.2, 130.7, 129.2, 129.0, 128.9, 128.7, 128.3, 128.3, 128.2, 124.1, 122.8, 121.0, 111.5, 104.6, 71.1, 68.8, 52.5. HRMS (ESI+) calcd. for C28H25N2O3 [M+H] 437.1865, found 437.1860.

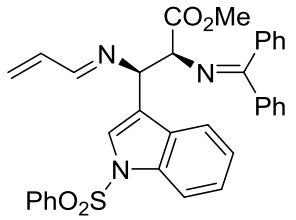
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 20/1/0.1, 254 nm absorbance). Major enantiomer (tR = 20.5 min), minor enantiomer (tR = 26.8 min): er = 89 :11.



Peak No.	Peak Name	Result ()	Time (min)	Offset (min)	Area (counts)	Sep. Code	1/2 (sec)	Status Codes
1		49.5931	21.512	0.000	2833231	BB	33.1	U
2		50.4069	27.979	0.000	2879720	BB	39.9	
	Totals:	100.0000		0.000	5712951			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		89.7737	20.489	0.000	16704058	BB	31.5	
2		10.2263	26.760	0.000	1902784	BB	40.3	
	Totals:	100.0000		0.000	18606842			

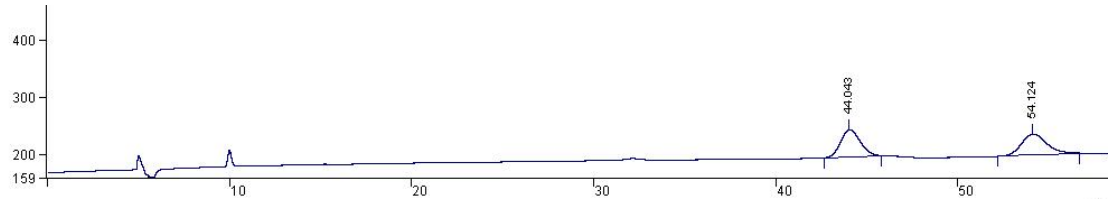


Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3 -(1-(phenylsulfonyl)-1H-indol-3-yl)propanoate (3p)

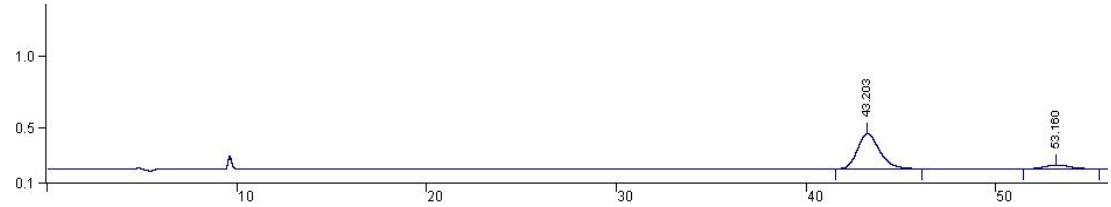
The reaction was performed with *N*-allyl imine (170.0 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 42 h at 4^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 8/92/1) gave product (178 mg, 62%) as a colorless oil. α_D^{25} = -79.3 (*c* = 2.0, $CHCl_3$). IR: (neat) 3058, 1741, 1650, 1619, 1447 cm^{-1}; ^1H NMR (500 MHz, d-$CDCl_3$) δ 8.03 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 8.5 Hz, 1H), 7.81 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.59 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.54 (s, 1H), 7.42-7.46 (m, 2H), 7.34-7.36 (m, 3H), 7.25-7.32 (m, 6H), 7.08 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 7.0 Hz, 2H), 6.47-6.54 (m, 1H), 5.71 (d, *J* = 10.5 Hz, 1H), 5.63 (d, *J* = 17.5 Hz, 1H), 5.13 (d, *J* = 7.5 Hz, 1H), 4.55 (d, *J* = 7.5 Hz, 1H), 3.47 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.0, 169.2, 165.1, 139.7, 138.2, 137.2, 136.1, 135.2, 133.8, 133.5, 130.7, 129.4, 129.3, 129.2, 128.8, 128.4, 128.2, 128.1, 127.0, 124.8, 124.4, 123.3, 121.7, 120.7, 113.5, 69.8, 69.7, 52.2. HRMS (ESI+) calcd. for C34H29N3O4S [M+Na] 598.1776, found 598.1771.

Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N =

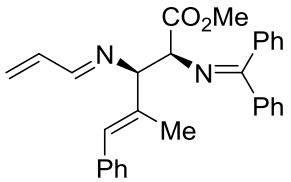
20/1/0.1, 254 nm absorbance). Major enantiomer (tR = 43.2 min), minor enantiomer (tR = 53.2 min): er = 89 :11.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.1614	44.043	0.000	3574362	BB	74.8	
2		49.8386	54.124	0.000	3551360	BB	99.3	
	Totals:	100.0000		0.000	7125722			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		88.8054	43.203	0.000	19966292	BB	77.4	
2		11.1946	53.160	0.000	2516911	BB	89.8	
	Totals:	100.0000		0.000	22483203			

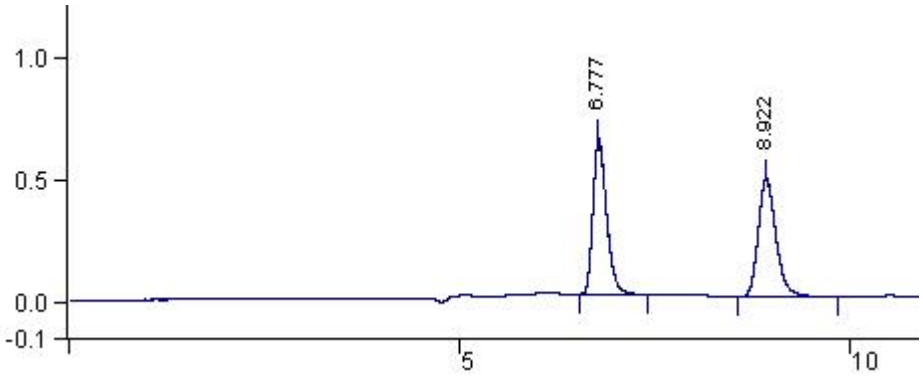


Methyl (2S,3R,E)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-4 -methyl-5-phenylpent-4-enoate (3q)

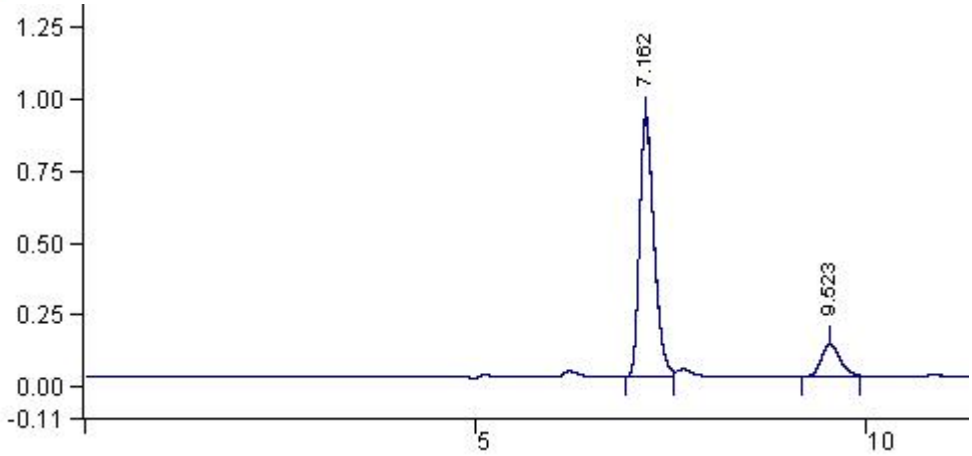
The reaction was performed with *N*-allyl imine (91.8 mg, 0.5 mmol), methyl glycinate (126 mg, 0.5 mmol), $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), (S,S)-Cy DIOP (16.2 mg, 0.03 mmol), 2,6-dimethylbenzoquinone (70 mg, 0.5 mmol) and Et_3N (50 mg, 0.5 mmol) in toluene (1.0 mL) for 72 h at 4^{o}C. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (162 mg, 74%) as a colorless oil. α_D^{25} = -36.8 (*c* = 2.0, $CHCl_3$). IR: (neat) 3056, 2950, 1742, 1614, 1492

cm^{-1}; ^{1}H NMR (500 MHz, d-$CDCl_3$) δ 8.05 (d, *J* = 9.0 Hz, 1H), 7.60-7.62 (m, 2H), 7.46-7.48 (m, 3H), 7.39-7.41 (m, 1H), 7.30-7.35 (m, 5H), 7.23-7.25 (m, 2H), 7.20-7.22 (m, 2H), 6.50-6.57 (m, 2H), 5.76 (d, *J* = 10.0 Hz, 1H), 5.70 (d, *J* = 17.0 Hz, 1H), 4.61 (d, *J* = 7.5 Hz, 1H), 4.42 (d, *J* = 7.5 Hz, 1H), 3.70 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 171.3, 164.7, 139.9, 137.7, 137.4, 137.2, 136.5, 130.5, 129.2, 129.1, 128.9, 128.6, 128.3, 128.2, 128.2, 128.1, 127.9, 126.6, 82.3, 69.3, 52.3, 15.2. HRMS (ESI+) calcd. for C29H28N2O2 [M+Na] 459.2033, found 459.2043.

Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 20/1/0.1, 254 nm absorbance). Major enantiomer (tR = 7.2 min), minor enantiomer (tR = 9.5 min): er = 86.5 :13.5.

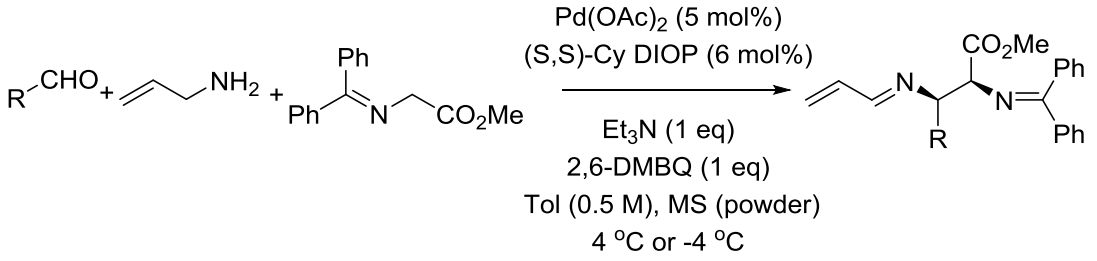


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.1027	6.777	0.000	7742906	BB	11.0	
2		49.8973	8.922	0.000	7711178	BB	14.3	
Totals:		100.0000		0.000	15454084			

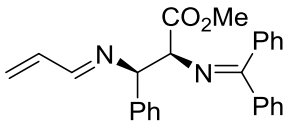


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		86.5055	7.162	0.000	11755970	BB	11.8	
2		13.4945	9.523	0.000	1833881	BB	15.4	
	Totals:	100.0000		0.000	13589851			

V. General procedure for the three-component AAA reactions:



An oven dried Pyrex microwave vial was charged with $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), (S,S)-Cy DIOP (10.1 mg, 0.018 mmol), 2,6-dimethylbenzoquinone (42 mg, 0.3 mmol) and molecular sieve (4 Å, 120 mg) was sealed with a rubber septa. The vial was evacuated and filled with nitrogen three times in an interval of 10 min. In a separate sealed nitrogen flushed vial, aldehyde (0.3 mmol), allyl amine (0.3 mmol) and glycinate **2e** (0.3 mmol) were dissolved in freshly distilled toluene (0.6 ml). The solution was cannulated to the microwave vial with palladium catalyst. Et_3N (30 mg, 0.3 mmol) was added to the resulting turbid solution and was allowed to stir at 4 ^oC or -4 ^oC for 35-60h. Upon completion (monitored by crude NMR), solvent was removed in vacuo and the residue was purified by flash chromatography over silica gel (pre-neutralized with 3% Et_3N in Hexanes), eluting with EtOAc / hexanes/ Et_3N, to give the product.



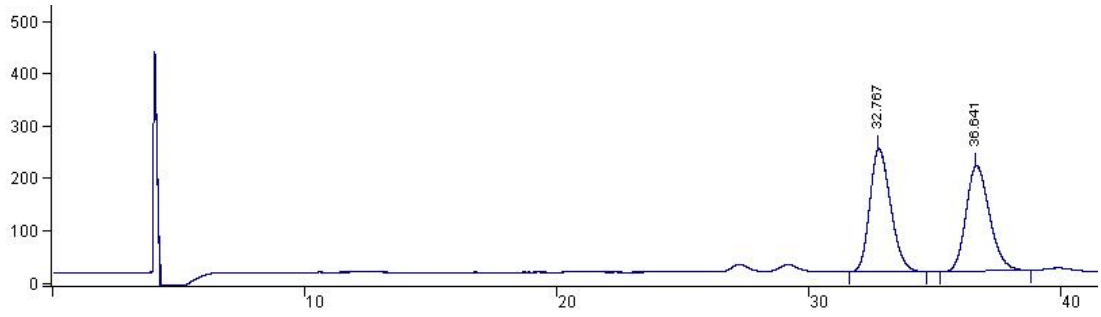
Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-phenyl propanoate (6a)

The reaction was performed with allyl amine (17.1 mg, 0.3 mmol), benzaldehyde (31.8 mg, 0.3 mmol), methyl glycinate (75.3 mg, 0.3 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol),

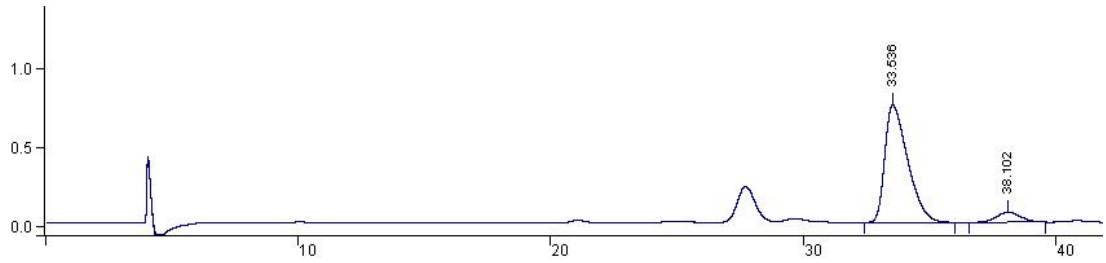
(S,S)-Cy DIOP (10.1 mg, 0.018 mmol), 2,6-dimethylbenzoquinone (40.8 mg, 0.3 mmol), Et_3N (30.3 mg, 0.3 mmol) and molecular sieve (4 Å, 120 mg) in toluene (0.6 mL) for 36 h at 4°C. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (69 mg, 58%) as a colorless oil. α_D^{25} = -32.4 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, d-$CDCl_3$) δ 8.06 (d, *J* = 9.0 Hz, 1H), 7.61 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.45-7.47 (m, 3H), 7.39-7.42 (m, 1H), 7.32-7.35 (m, 4H), 7.27-7.29 (m, 2H), 7.23-7.25 (m, 1H), 7.08-7.10 (m, 2H), 6.51-6.58 (m, 1H), 5.73 (d, *J* = 10.5 Hz, 1H), 5.67 (d, *J* = 17.5 Hz, 1H), 4.91 (d, *J* = 8.0 Hz, 1H), 4.58 (d, *J* = 8.0 Hz, 1H), 3.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3, 170.9, 164.7, 140.2, 139.8, 137.1, 136.5, 130.6, 129.1, 128.9, 128.6, 128.5, 128.3, 128.3, 128.2, 127.9, 127.8, 78.0, 72.0, 52.2.

The analytical data of the compound **6a** was in complete agreement with compound **3b**.

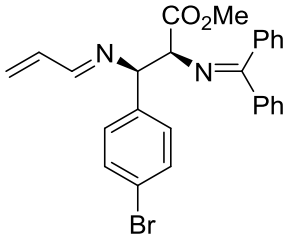
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 100/1/0.1, 254 nm absorbance). Major enantiomer (tR = 33.5 min), minor enantiomer (tR = 38.1 min): er = 92:8.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.9083	32.767	0.000	13604943	BB	56.7	
2		49.0917	36.641	0.000	13119480	BB	61.4	
	Totals:	100.0000		0.000	26724423			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		91.6614	33.536	0.000	47177608	BB	66.1	
2		8.3386	38.102	0.000	4291805	BB	63.9	
	Totals:	100.0000		0.000	51469413			

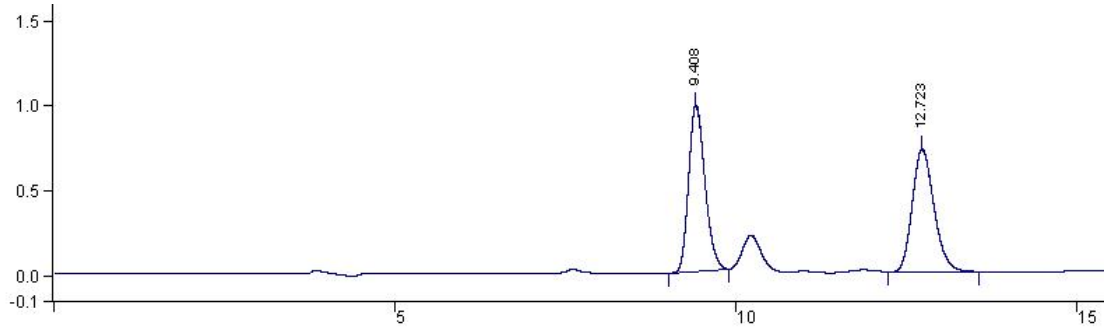


Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-(4-bromophenyl)propanoate (6b)

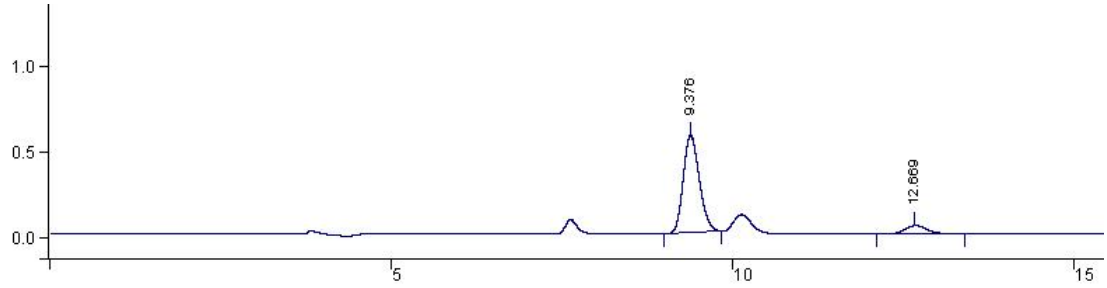
The reaction was performed with allyl amine (17.1 mg, 0.3 mmol), 4-bromobenzaldehyde (55.5 mg, 0.3 mmol), methyl glycinate (75.3 mg, 0.3 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), (S,S)-Cy DIOP (10.1 mg, 0.018 mmol), 2,6-dimethylbenzoquinone (40.8 mg, 0.3 mmol), Et_3N (30.3 mg, 0.3 mmol) and molecular sieve (4 Å, 120 mg) in toluene (0.6 mL) for 42 h at -4 ^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (99.8 mg, 70%) as a colorless oil. α_D^{25} = -101.2 (*c* = 3.0, $CHCl_3$). ^1H NMR (500 MHz, d-$CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 2H), 7.45-7.47 (m, 3H), 7.39-7.41 (m, 3H), 7.32-7.35 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.08-7.10 (m, 2H), 6.48-6.58 (m, 1H), 5.73 (d, *J* = 10.0 Hz, 1H), 5.66 (d, *J* = 17.0 Hz, 1H), 4.85 (d, *J* = 8.0 Hz, 1H), 4.51 (d, *J* = 8.0 Hz, 1H), 3.58 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.6, 170.7, 165.2, 142.6, 139.6, 137.0, 136.3, 131.6, 131.3, 130.8, 130.0, 129.1, 129.0, 128.6, 128.1, 126.9, 122.5, 77.1, 71.7, 52.3.

The analytical data of the compound **6b** was in complete agreement with compound **3g**.

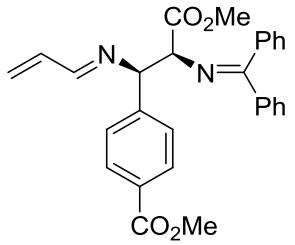
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 20/1/0.1, 254 nm absorbance). Major enantiomer (tR = 9.4 min), minor enantiomer (tR = 12.7 min): er = 90 :10.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.5039	9.408	0.000	16373066	BB	15.6	
2		49.4961	12.723	0.000	16046370	BB	20.4	
	Totals:	100.0000		0.000	32419436			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		89.7225	9.376	0.000	9443265	BB	15.3	
2		10.2775	12.669	0.000	1081702	BB	20.3	
	Totals:	100.0000		0.000	10524967			

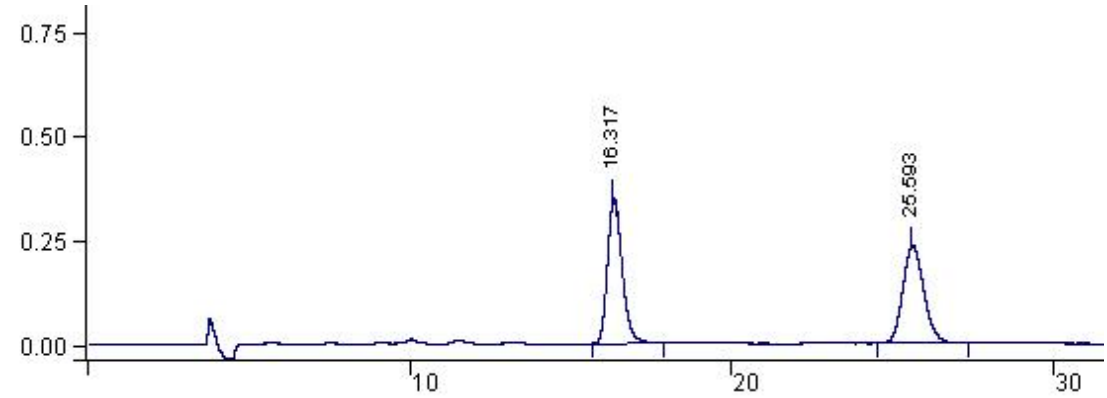


Methyl 4-((1R,2S)-1-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-methoxy-3-oxopropyl)benzoate (6c)

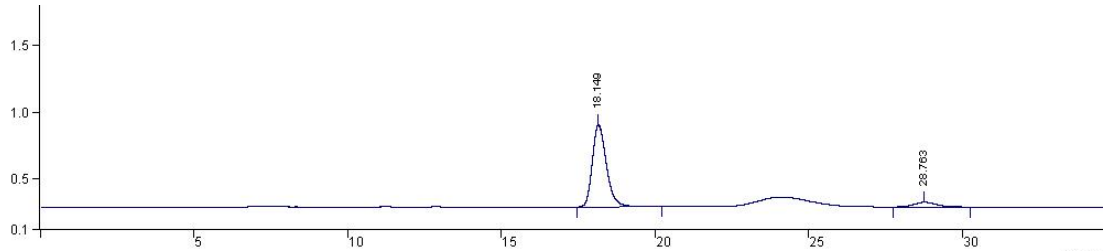
The reaction was performed with allyl amine (17.1 mg, 0.3 mmol), methyl 4-formylbenzoate (49.3 mg, 0.3 mmol), methyl glycinate (75.3 mg, 0.3 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), (S,S)-Cy DIOP (10.1 mg, 0.018 mmol), 2,6-dimethylbenzoquinone (40.8 mg, 0.3 mmol), Et_3N (30.3 mg, 0.3 mmol) and molecular sieve (4 Å, 120 mg) in toluene (0.6 mL) 40 h at -4^{o}C. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 10/90/1) gave product (87.3 mg, 68%) as a colorless oil. α_D^{25} = -95.9 (*c* = 2.0, $CHCl_3$). ^{1}H NMR (500 MHz, d-$CDCl_3$) δ 8.05 (d, *J* = 9.0 Hz, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.44-7.46 (m, 3H), 7.39-7.43 (m, 3H), 7.31-7.35 (m, 2H), 7.05-7.08 (m, 2H), 6.51-6.59 (m, 1H), 5.75 (d, *J* = 10.5 Hz, 1H), 5.69 (d, *J* = 17.5 Hz, 1H), 4.96 (d, *J* = 7.5 Hz, 1H), 4.55 (d, *J* = 7.5 Hz, 1H), 3.90 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.1, 170.6, 167.1, 165.2, 145.4, 139.6, 137.0, 136.3, 130.7, 129.8, 129.5, 129.1, 128.9, 128.6, 128.3, 128.2, 128.1, 128.1, 77.5, 71.2, 52.3.

The analytical data of the compound **6c** was in complete agreement with compound **3c**.

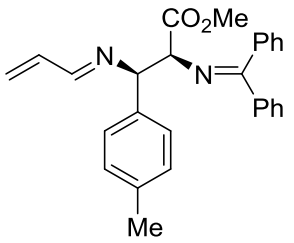
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 20/1/0.1, 254 nm absorbance). Major enantiomer (tR = 18.1 min), minor enantiomer (tR = 28.8 min): er = 92:8.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.9142	16.317	0.000	11111619	BB	29.4	
2		49.0858	25.593	0.000	10712607	BB	42.1	
	Totals:	100.0000		0.000	21824226			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		92.0109	18.149	0.000	19624650	BB	29.3	
2		7.9891	28.763	0.000	1703957	BB	45.3	
	Totals:	100.0000		0.000	21328607			



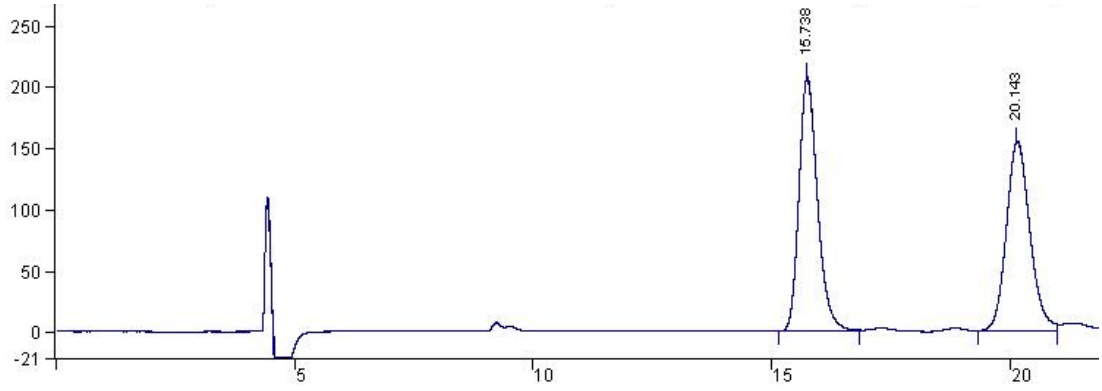
Methyl (2S,3R)-3-(((E)-allylidene)amino)-2-((diphenylmethylene)amino)-3-(4-methylphenyl)propanoate (6d)

The reaction was performed with allyl amine (17.1 mg, 0.3 mmol), 4-methylbenzaldehyde (36.1 mg, 0.3 mmol), methyl glycinate (75.3 mg, 0.3 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), (S,S)-Cy DIOP (10.1 mg, 0.018 mmol),

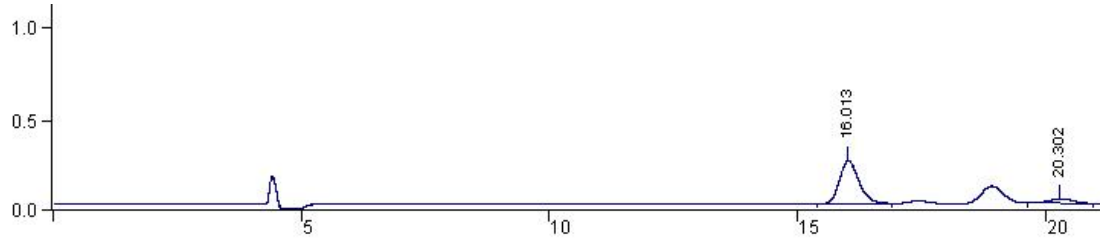
2,6-dimethylbenzoquinone (40.8 mg, 0.3 mmol), Et_3N (30.3 mg, 0.3 mmol) and molecular sieve (4 Å, 120 mg) in toluene (0.6 mL) for 40 h at 4°C. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (64 mg, 52%) as a colorless oil. α_D^{25} = -55.4 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, d-$CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.42-7.44 (m, 3H), 7.35-7.38 (m, 1H), 7.28-7.33 (m, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.04-7.10 (m, 4H), 6.45-6.54 (m, 1H), 5.68 (d, *J* = 10.0 Hz, 1H), 5.63 (d, *J* = 17.2 Hz, 1H), 4.84 (d, *J* = 8.0 Hz, 1H), 4.54 (d, *J* = 8.0 Hz, 1H), 3.52 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 171.0, 164.5, 139.9, 137.3, 137.2, 137.1, 136.5, 130.5, 129.2, 129.1, 128.8, 128.5, 128.3, 128.1, 128.1, 127.8, 77.7, 72.1, 52.1, 21.3.

The analytical data of the compound **6d** was in complete agreement with compound **3e**.

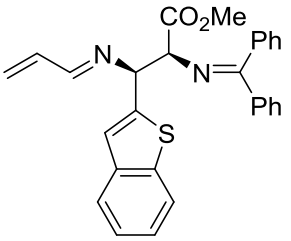
Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 40/1/0.1, 254 nm absorbance). Major enantiomer (tR = 16.0 min), minor enantiomer (tR = 20.3 min): er = 88.5 :11.5.



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		51.2319	15.738	0.000	5603092	BB	24.8	
2		48.7681	20.143	0.000	5333625	BB	31.1	
	Totals:	100.0000		0.000	10936717			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		88.4517	16.013	0.000	6268478	BB	25.1	
2		11.5483	20.302	0.000	818417	BB	30.7	
	Totals:	100.0000		0.000	7086895			

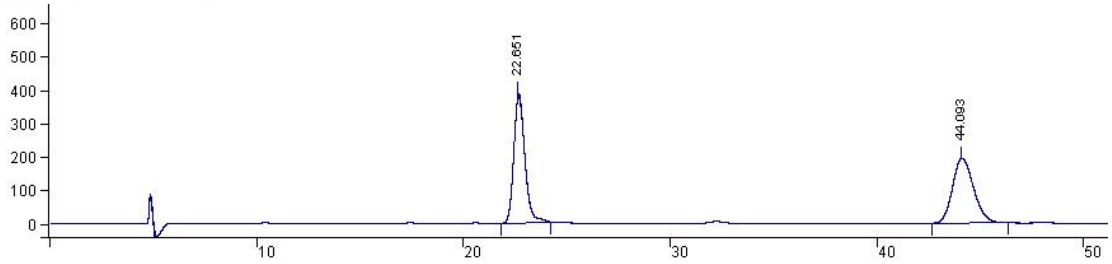


Methyl (2S,3S)-3-(((E)-allylidene)amino)-3-(benzo[b]thiophen-2-yl)-2-((diphenyl methylene)amino)propanoate (6e)

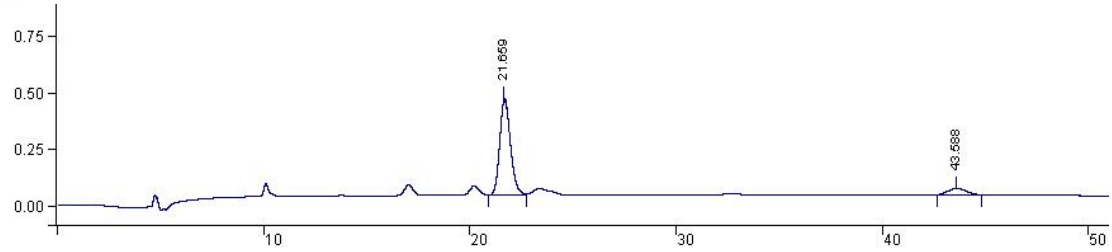
The reaction was performed with allyl amine (17.1 mg, 0.3 mmol), benzo[b]thiophene-2-carboxaldehyde (48.7 mg, 0.3 mmol), methyl glycinate (75.3 mg, 0.3 mmol), $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), (S,S)-Cy DIOP (10.1 mg, 0.018 mmol), 2,6-dimethylbenzoquinone (40.8 mg, 0.3 mmol), Et_3N (30.3 mg, 0.3 mmol) and molecular sieve (4 Å, 120 mg) in toluene (0.6 mL) for 62 h at 4 ^oC. After removing the solvent, purification by flash chromatography (EtOAC / hexanes /Et_3N = 5/95/1) gave product (82 mg, 60%) as a colorless oil. α_D^{25} = -43.4 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, d-$CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.62-7.65 (m, 2H), 7.42-7.44 (m, 3H), 7.38-7.43 (m, 1H), 7.31-7.34 (m, 2H), 7.23-7.30 (m, 3H), 7.13-7.15 (m, 2H), 6.56-6.62 (m, 1H), 5.74 (d, *J* = 10.0 Hz, 1H), 5.68 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 7.6 Hz, 1H), 4.61 (d, *J* = 7.6 Hz, 1H), 3.60 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8, 170.6, 165.4, 143.9, 140.0, 139.6, 139.4, 136.9, 136.2, 130.7, 129.2, 128.9, 128.6, 128.2, 128.1, 124.2, 124.1, 123.5, 122.4, 121.6, 72.9, 71.8, 52.4.

The analytical data of the compound **6e** was in complete agreement with compound **3n**.

Enantiomeric excess was determined by using HPLC with a chiral stationary phase. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 40/1/0.1, 254 nm absorbance). Major enantiomer (tR = 21.7 min), minor enantiomer (tR = 43.6 min): er = 90 :10.

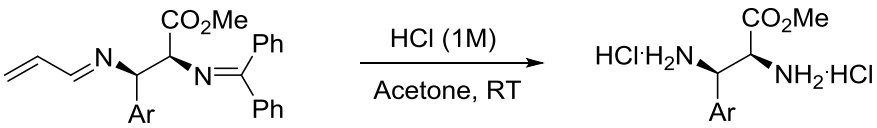


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.9011	22.651	0.000	14306732	BB	34.4	
2		49.0989	44.093	0.000	13800196	BB	67.6	
	Totals:	100.0000		0.000	28106928			



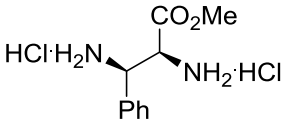
Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		89.7569	21.659	0.000	15366331	BB	33.9	
2		10.2431	43.588	0.000	1753606	BB	61.4	
	Totals:	100.0000		0.000	17119937			

VI. General method for synthesis of vicinal diamino derivatives:



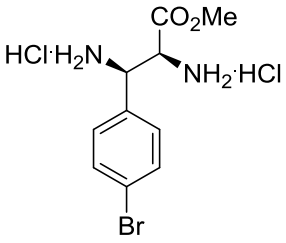
To a solution of 1-aza diene (0.3 mmol) in acetone (3 ml) was added HCl (1M, 1.2 mmol) dropwised at 0 ^oC. The reaction mixture was stirred at room temperature for 1 h.

The acetone was removed in vacuo and the residue was washed with Et_2O (3 ml) twice. The residue was dried in vacuo to afford the product as a solid.



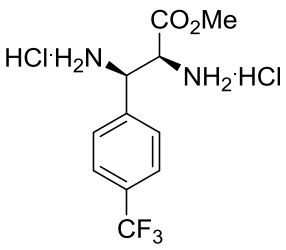
Methyl (2S,3R)-2,3-diamino-3-phenylpropanoate dihydrochloride (7a)

Light yellow solid, 74 mg, 92% yield, Mp = 202-204 ^{o}C. α_D^{25} = +11.0 (free amine, *c* = 1.0, $CHCl_3$). IR: (neat) 3644, 3331, 3263, 1754, 1528, 1422 cm^{-1}; ^{1}H NMR (500 MHz, d-DMSO) δ 9.57 (br, 3H), 9.26 (br, 3H), 7.54-7.56 (m, 2H), 7.46-7.48 (m, 3H), 5.04 (d, *J* = 7.5 Hz, 1H), 4.82 (d, *J* = 7.5 Hz, 1H), 3.63 (s, 3H). ^{13}C NMR (125 MHz, d-DMSO) δ 166.4, 131.4, 129.9, 128.9, 128.2, 54.5, 54.3, 53.4. HRMS (ESI+) calcd. for C10H16Cl2N2O2 [M-2HCl+H] 195.1132, found 195.1128.



Methyl (2S,3R)-2,3-diamino-3-(4-bromophenyl)propanoate dihydrochloride (7b)

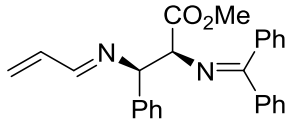
white solid, 93 mg, 90% yield, Mp = 214-217 ^{o}C. α_D^{25} = +18.6 (free amine, *c* = 1.0, $CHCl_3$). IR: (neat) 3648, 3255, 2069, 1742, 1522 cm^{-1}; ^{1}H NMR (500 MHz, d-CD_3OD) δ 7.75 (d, *J* = 8.5Hz, 2H), 7.49 (d, *J* = 8.5Hz, 2H), 5.15 (d, *J* = 4.5 Hz, 1H), 4.97 (d, *J* = 4.5 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (125 MHz, d- CD_3OD) δ 167.2, 134.1, 131.4, 130.2, 126.1, 55.3, 54.8, 54.6. HRMS (ESI+) calcd. for C10H15BrCl2N2O2 [M-2HCl+H] 273.0231, found 273.0233.



Methyl (2S,3R)-2,3-diamino-3-(4-trifluromethylphenyl)propanoate dihydrochloride (7c)

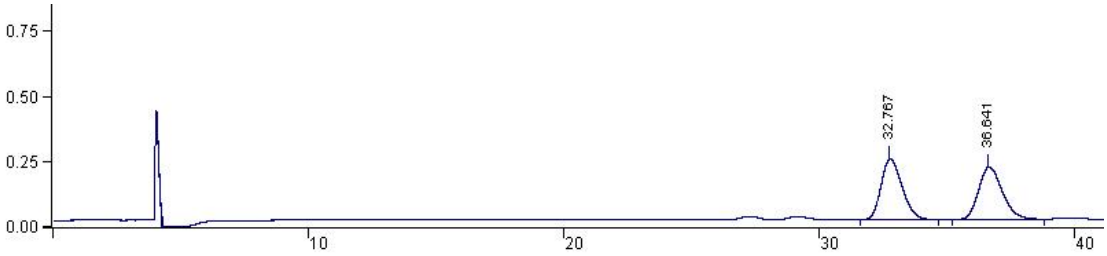
Light yellow solid, 90 mg, 90% yield, Mp = 221-225 ^{o}C. α_D^{25} = +17.4 (free amine, *c* = 1.0, $CHCl_3$). IR: (neat) 3661, 3355, 2078, 1740, 1536 cm^{-1}; ^{1}H NMR (500 MHz, d-CD_3OD) δ 7.89 (d, *J* = 8.0Hz, 2H), 7.81 (d, *J* = 8.0Hz, 2H), 5.32 (d, *J* = 5.0 Hz, 1H), 5.06 (d, *J* = 5.0 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (125 MHz, d- CD_3OD) δ 167.1, 135.5, 133.5 (q, *J* = 32 Hz), 130.5 (d, *J* = 12 Hz), 127.8, 125.1 (d, *J* = 271 Hz), 55.4, 54.9, 54.7. HRMS (ESI+) calcd. for C11H15F3Cl2N2O2 [M-2HCl+H] 263.1001, found 263.1002.

Preparation of the product 3b in gram scale:

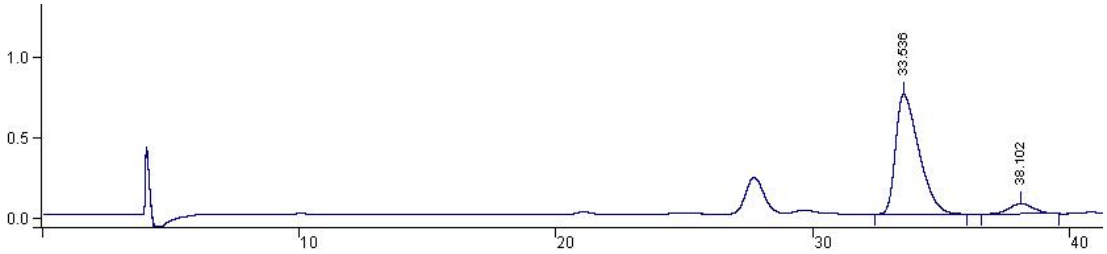


An oven dried Pyrex microwave vial was charged with $Pd(OAc)_2$ (56 mg, 0.25 mmol), (S,S)-Cy DIOP (162 mg, 0.3 mmol), 2,6-dimethylbenzoquinone (700 mg, 5 mmol) and was sealed with a rubber septa. The vial was evacuated and filled with nitrogen three times in an interval of 10 min. In a separate sealed nitrogen flushed vial, methyl glycinate (1.25 g, 5 mmol) and *N*-allyl imine (750 mg, 5 mmol) were taken in freshly distilled toluene (10 ml). The solution was cannulated to the microwave vial with palladium catalyst. Et_3N (500 mg, 5 mmol) was added to the resulting turbid solution and was allowed to stir at 4 ^{o}C for 40 h. Upon completion (monitored by crude NMR), solvent was removed in vacuo and the residue was purified by flash chromatography over silica gel (pre-neutralized with 3% Et_3N in Hexanes), eluting with EtOAc / hexanes/ Et_3N, to give the product **3b** 1.33 g in 67% yield.

Enantiomeric excess was determined by using HPLC. Stationary phase (AD column, flow rate = 1.0 mL/min, eluent: Hept/*i*-PrOH/Et_3N = 100/1/0.1, 254 nm absorbance). Major enantiomer (tR = 33.5 min), minor enantiomer (tR = 38.1 min): er = 92:8.

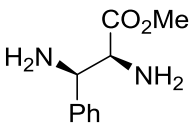


Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		50.9083	32.767	0.000	13604943	BB	56.7	
2		49.0917	36.641	0.000	13119480	BB	61.4	
	Totals:	100.0000		0.000	26724423			



Peak No.	Peak Name	Result ()	Ret. Time (min)	Time Offset (min)	Area (counts)	Sep. Code	Width 1/2 (sec)	Status Codes
1		91.6614	33.536	0.000	47177608	BB	66.1	
2		8.3386	38.102	0.000	4291805	BB	63.9	
	Totals:	100.0000		0.000	51469413			

Determination of relative and absolute configuration of AAA products:



The relative stereochemistry of both diastereomers were determined by comparing the ^{1}H NMR spectra of diamines **7a** with the ones obtained from literature.[4] The free diamines were obtained by dissolving the diaminium salts in 1 N NaOH solution and extraction with CH_2Cl_2 for three times.

Major diastereomer: ^{1}H NMR (500 MHz, d-$CDCl_3$) δ 7.28-7.36 (m, 5H), 4.30 (d, *J* = 4.5 Hz, 1H), 3.67 (s, 3H), 3.65 (d, *J* = 4.5 Hz, 1H),1.71 (brs, 4H). ^{13}C NMR (125 MHz,

d-$CDCl_3$) δ 174.6, 142.8, 128.7, 127.6, 126.9, 61.0, 58.4, 52.3.

The spectra data of the compound was in complete agreement with the literature of *cis*-diamine.[4a]

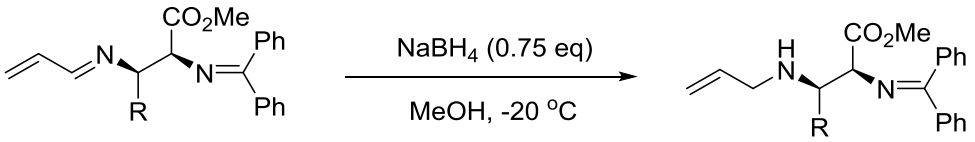
Minor diastereomer: ^{1}H NMR (500 MHz, d-$CDCl_3$) δ 7.28-7.36 (m, 5H), 4.25 (d, *J* = 6.0 Hz, 1H), 3.71 (d, *J* = 6.0 Hz, 1H), 3.70 (s, 3H).

The spectra data of the compound was in complete agreement with the literature of *trans*-diamine.[4b]

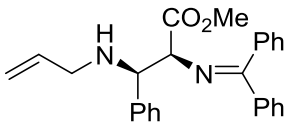
The absolute configuration was established by its optical rotation of α_D^{25}= +11.0^o (*c*= 1.0, $CHCl_3$, 92:8 er) which agrees with that reported for the *S,R*-isomer α_D^{25}= +16.0^o (*c*= 1.0, $CHCl_3$, >99%ee).[5]

VII. Structural Derivatization of AAA products

General procedure for reduction with $NaBH_4$:



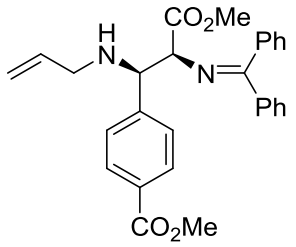
To a solution of 1-aza diene (0.3 mmol) in MeOH (1.5 ml) was added $NaBH_4$ (8.6 mg, 0.21 mmol) at -20 ^{o}C. The reaction mixture was stirred for 15 min. The methanol was removed in vacuo and the residue was washed with DCM (3 ml) twice. The dichloromethane solution was dried in vacuo and purified by flashing chromatography.



Methyl (2S,3R)-3-(allylamino)-2-((diphenylmethylene)amino)-3-Phenylpropanoate (8a)

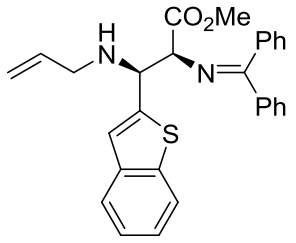
Colorless oil. 74 mg, 62% yield. α_D^{25}= -79.7 (*c*= 1.2, $CHCl_3$). IR: (neat) 3361, 3061, 2952, 1741, 1448 cm^{-1}; ^{1}H NMR (400 MHz, d-$CDCl_3$) δ 7.64 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.39-7.41 (m, 1H), 7.32-7.36 (m, 3H), 7.27-7.32 (m, 3H), 7.22-7.25 (m, 2H), 7.15-7.18

(m, 2H), 6.60 (d, *J* = 6.8 Hz, 2H), 5.82-5.92 (m, 1H), 5.09-5.15 (m, 1H), 5.04-5.07 (m, 1H), 4.44 (d, *J* = 4.8 Hz, 1H), 4.17 (d, *J* = 4.8 Hz, 1H), 3.64 (s, 3H), 3.20-3.26 (m, 1H), 2.99-3.05 (m, 1H). ^{13}C NMR (125 MHz, d-$CDCl_3$) δ 172.2, 171.6, 140.5, 139.3, 137.3, 136.2, 130.7, 129.1, 128.6, 128.5, 128.4, 128.3, 128.1, 127.6, 127.4, 115.8, 71.6, 64.4, 52.2, 49.6. HRMS (ESI+) calcd. for C26H26N2O2 [M+Na] 421.1870, found 421.1882.



Methyl 4-((1R,2S)-1-(allylamino)-2-((diphenylmethylene)amino)-3-methoxy-3-oxopropyl)benzoate (8b)

Colorless oil. 82 mg, 63% yield. α_D^{25}= -93.8 (*c*= 1.0, $CHCl_3$). IR: (neat) 3364, 3002, 2951, 1724, 1440 cm^{-1}; ^{1}H NMR (500 MHz, d-$CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.65 (dd, *J* = 8.5, 3.5 Hz, 2H), 7.47-7.52 (m, 1H), 7.42-7.45 (m, 1H), 7.35-7.38 (m, 3H), 7.30-7.32 (m, 3H), 6.64 (d, *J* = 7.0 Hz, 2H), 5.84-5.92 (m, 1H), 5.11-5.15 (m, 1H), 5.07-5.10 (m, 1H), 4.52 (d, *J* = 5.5 Hz, 1H), 4.21 (d, *J* = 5.5 Hz, 1H), 3.92 (s, 3H), 3.68 (s, 3H), 3.23-3.27 (m, 1H), 3.01-3.06 (m, 1H). ^{13}C NMR (125 MHz, d-$CDCl_3$) δ 172.6, 171.3, 167.2, 146.3, 139.1, 137.0, 136.0, 130.9, 129.7, 129.3, 129.1, 128.8, 128.6, 128.3, 128.2, 127.5, 116.1, 71.2, 64.1, 52.4, 52.3, 49.7. HRMS (ESI+) calcd. for C28H28N2O4 [M+H] 457.2122, found 457.2113.

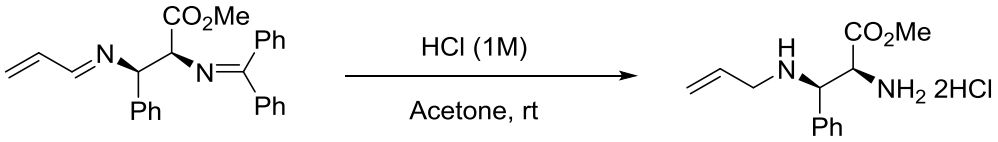


Methyl (2S,3S)-3-(allylamino)-3-(benzo[b]thiophen-2-yl)-2-((diphenylmethylene) amino)propanoate (8c)

Colorless oil. 79 mg, 58% yield. α_D^{25}= -77.1 (*c*= 1.0, $CHCl_3$). IR: (neat) 3338, 3060, 2918, 1741, 1625 cm^{-1}; ^{1}H NMR (400 MHz, d-$CDCl_3$) δ 7.71-7.75 (m, 3H), 7.66 (dd, *J*

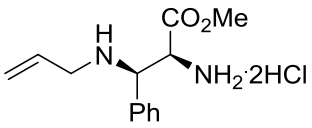
= 7.2, 1.2 Hz, 1H), 7.42-7.45 (m, 1H), 7.38-7.40 (m, 2H), 7.34-7.36 (m, 1H), 7.30-7.33 (m, 3H), 7.27-7.29 (m, 1H), 7.23-7.26 (m, 1H), 6.89 (d, *J* = 6.8 Hz, 2H), 5.82-5.92 (m, 1H), 5.15-5.19 (m, 1H), 5.08-5.11 (m, 1H), 4.75 (d, *J* = 4.0 Hz, 1H), 4.38 (d, *J* = 4.0 Hz, 1H), 3.68 (s, 3H), 3.31-3.36 (m, 1H), 3.10-3.15 (m, 1H). ^{13}C NMR (100 MHz, d-$CDCl_3$) δ 173.3, 171.2, 146.5, 140.2, 139.5, 139.3, 137.1, 136.2, 130.9, 129.4, 128.8, 128.7, 128.3, 127.6, 124.2, 124.0, 123.4, 122.6, 122.5, 116.3, 70.8, 60.4, 52.5, 49.5. HRMS (ESI+) calcd. for C28H26N2O2S [M+H] 455.1788, found 455.1779.

Derivatization procedure for product 8a:



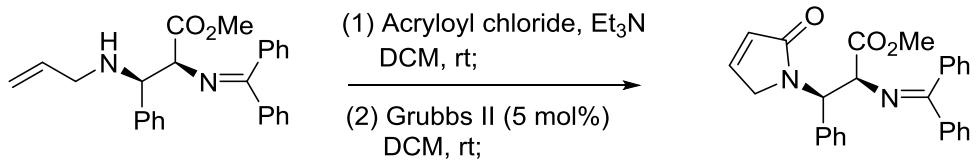
8a **9**

To a solution of 1-aza diene **8a** (40mg, 0.1 mmol) in acetone (1 ml) was added HCl (1M, 0.4 mmol) dropwised at 0 ^{o}C. The reaction mixture was stirred at room temperature for 1 h. The acetone was removed in vacuo and the residue was washed with Et_2O (3 ml) twice. The residue was dried in vacuo to afford the product as a white solid.



Methyl (2S,3R)-3-(allylamino)-2-amino-3-phenylpropanoate dihydrochloride (9)

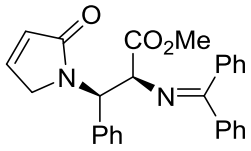
White solid, 22 mg, 95% yield, Mp = 210-212 ^{o}C. α_D^{25}= +15.0 (free amine, *c*= 0.2, $CHCl_3$). IR: (neat) 3318, 2921, 2853, 1737, 1450 cm^{-1}; ^{1}H NMR (500 MHz, d-CD_3OD) δ 7.57-7.62 (m, 3H), 7.45-7.47 (m, 2H), 5.99-6.07 (m, 1H), 5.56 (d, *J* = 10.0 Hz, 1H), 5.49 (d, *J* = 17.0 Hz, 1H), 5.03 (d, *J* = 4.5 Hz, 1H), 4.94 (d, *J* = 5.0 Hz, 1H), 3.98 (s, 3H). ^{13}C NMR (125 MHz, d-CD_3OD) δ 167.3, 132.7, 131.4, 130.2, 128.7, 128.2, 126.0, 61.0, 54.6, 50.6. HRMS (ESI+) calcd. for C13H18ClN2O2 [M-2HCl+H] 235.1441, found 235.1441.



8a **10**

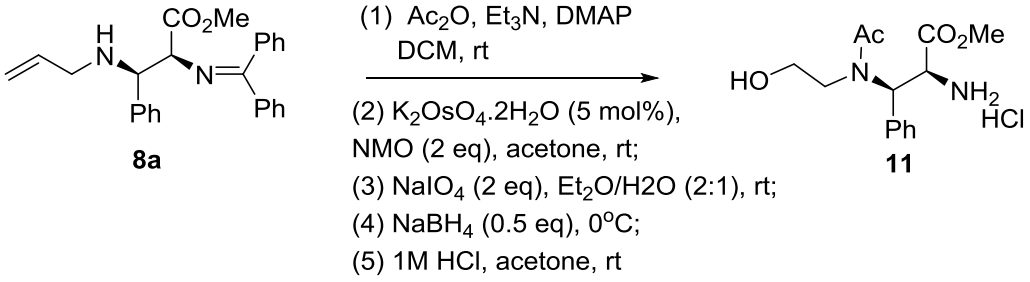
To a solution of allyl amine substrate **8a** (40 mg, 0.1 mmol) in DCM (1 ml) was added acryloyl chloride (9 mg, 0.1 mmol) dropwised at 0 ^{o}C. The reaction mixture was stirred at room temperature for 1 h. The reaction mixture was filtered through a short pad of silica gel and washed with DCM (5 ml). The solvent was removed in vacuo and the residue was used directly for the next step.

To a solution of the above residue in degassed DCM (3 ml) was added Grubbs II cat (4.2 mg, 0.005 mmol) under argon protection. The reaction mixture was stirred at room temperature for 6h. The reaction mixture was filtered through a short pad of Celite and washed with DCM (5 ml). The residue was dried in vacuo and purified by flashing chromatography.



Methyl (2S,3R)-2-((diphenylmethylene)amino)-3-(2-oxo-2,5-dihydro-1H-pyrrol -1-yl)-3-phenylpropanoate (10)

Colorless oil, 31 mg, 73% yield over two steps. α_D^{25}= -98.6 (*c*= 1.0, $CHCl_3$). IR: (neat) 3059, 2922, 1742, 1689, 1621, 1445 cm^{-1}; ^{1}H NMR (400 MHz, d-$CDCl_3$) δ 7.55 (dd, *J* = 8.4, 1.6 Hz, 2H), 7.44 (dd, *J* = 5.6, 1.2 Hz, 2H), 7.38-7.40 (m, 1H), 7.30-7.34 (m, 2H), 7.22-7.26 (m, 4H), 7.14-7.17 (m, 2H), 7.04-7.06 (m, 1H), 7.01-7.03 (m, 2H), 6.16 (d, *J* = 6.0 Hz, 1H), 6.06 (d, *J* = 5.6 Hz, 1H), 4.85 (d, *J* = 6.0 Hz, 1H), 4.31 (dt, *J* = 20.8, 2.0 Hz, 1H), 3.99 (dt, *J* = 20.4, 2.0 Hz, 1H), 3.62 (s, 3H). ^{13}C NMR (100 MHz, d-$CDCl_3$) δ 172.6, 171.7, 170.9, 144.1, 139.7, 137.9, 135.9, 130.8, 129.3, 129.3, 128.8, 128.8, 128.4, 128.1, 127.9, 127.3, 68.0, 57.1, 52.6, 52.1. HRMS (ESI+) calcd. for C27H24N2O3 [M+H] 425.1860, found 425.1849.



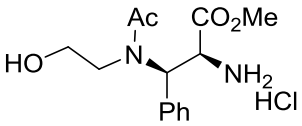
To a solution of allyl amine substrate **8a** (40 mg, 0.1 mmol) in CH_2Cl_2 (0.5 ml) was added acetic anhydride (15 mg, 0.15 mmol), DMAP (1.2 mg, 0.01 mmol) and Et_3N (30 mg, 0.3 mmol) at rt. The reaction mixture was stirred at rt for 6h. Water was added to the reaction mixture and it was extracted with EtOAc (10ml X 3). The organic layers were dried by Na_2SO_4 and evaporated under vacuum, and the residue was used for the next step.

A solution of $K_2OsO_4.2H_2O$ (2 mg, 0.005 mmol) and NMO (23.4 mg, 0.2 mmol) in water (0.1 ml) was added dropwise to a solution of **8a** acetate in acetone (1 ml). The reaction was stirred for 4h at rt. $Na_2S_2O_4$ (1ml, 2M solution) was added, the mixture was stirred for 30 min and then filtered through a pad of Celite, the solvent was removed in vacuo.

The crude product was dissolved in Et_2O/H_2O (1ml, 2:1). $NaIO_4$ (43 mg, 0.2 mmol) was added, and the reaction mixture was vigorously stirred for 1h at rt. Water (5 ml) and EtOAc (5 ml) was added, the aqueous layer was separated and extracted with EtOAc (3 X 5 ml). The organic layers were dried by Na_2SO_4 and concentrated in vacuo.

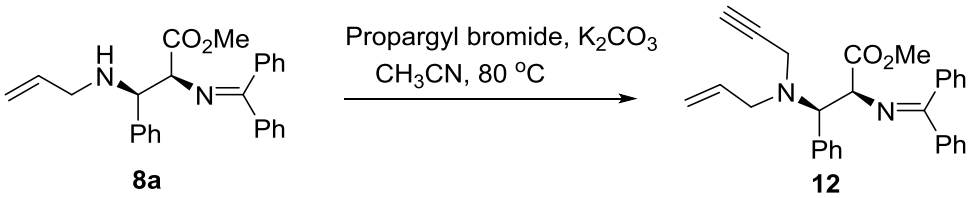
To a solution of the crude residue in MeOH (0.5 ml) was added $NaBH_4$ (2 mg, 0.05 mmol) at 0 ^oC. The reaction mixture was stirred for 5 min. The methanol was removed in vacuo and the residue was washed with DCM (3 ml) twice. The residue was dried in vacuo.

The residue was dissolved in acetone (1 ml) was added HCl (1M, 0.4 mmol) dropwised at 0 ^oC. The reaction mixture was stirred at room temperature for 1 h. The acetone was removed in vacuo and the residue was washed with Et_2O (3 ml) twice. The residue was dried in vacuo to afford the product as a white solid.



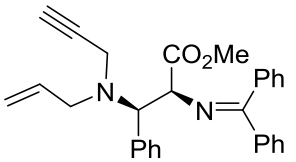
Methyl (2S,3R)-2-amino-3-(N-(2-hydroxyethyl)acetamido)-3-phenylpropanoate (**11**)

White solid, mp = 200-202 ^{o}C. 17 mg, 55% yield over five steps. α_D^{25}= 13.8 (*c*= 1.0, $CHCl_3$). IR: (neat) 3296, 3060, 2950, 2816, 1740, 1623, 1446 cm^{-1}; ^{1}H NMR (500 MHz, d-CD_3OD) δ 7.48-7.54 (m, 5H), 5.14 (d, *J* = 7.0 Hz, 1H), 4.76 (d, *J* = 7.0 Hz, 1H), 3.79-3.84 (m, 2H), 3.65 (s, 3H), 3.05-3.09 (m, 2H), 2.09 (s, 3H). ^{13}C NMR (125 MHz, d-CD_3OD) δ 174.3, 170.1, 131.9, 131.5, 130.6, 129.9, 68.9, 65.9, 64.2, 57.3, 56.0, 22.4. HRMS (ESI+) calcd. for C14H20N2O4 [M-HCl+Na] 303.1321, found 303.1311.



8a **12**

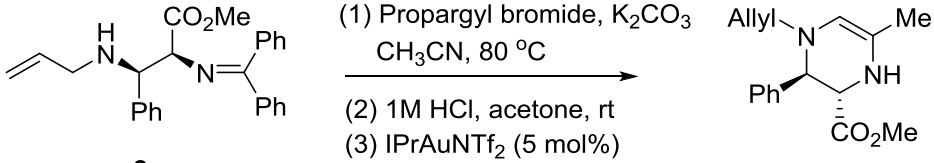
To a solution of allyl amine substrate **8a** (40 mg, 0.1 mmol) in CH_3CN (0.5 ml) was added propargyl bromide (30 mg, 80% wt in toluene, 0.2 mmol) and K_2CO_3 (70 mg, 0.5 mmol) at rt. The reaction mixture was stirred at 80 ^{o}C overnight. The reaction mixture was cooled to rt and quenched with water (5 ml). The reaction mixture was then extracted with ethyl acetate (5 ml) three times. The organic layers were dried with Na_2SO_4, and removed in vacuo and the residue was purified by flashing chromatography.



Methyl (2S,3R)-3-(allyl(prop-2-yn-1-yl)amino)-2-((diphenylmethylene)amino) -3-phenylpropanoate (12)

Colorless oil, 37 mg, 85% yield. α_D^{25}= -63.1 (*c*= 1.0, $CHCl_3$). IR: (neat) 3296, 3060, 2950, 2816, 1740, 1623, 1446 cm^{-1}; ^{1}H NMR (400 MHz, d-$CDCl_3$) δ 7.67-7.69 (m, 2H),

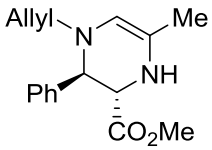
7.33-7.41 (m, 6H), 7.19-7.24 (m, 5H), 6.96 (d, *J* = 5.6 Hz, 2H), 5.74-5.84 (m, 1H), 5.21 (d, *J* = 17.2 Hz, 1H), 5.13 (d, *J* = 8.4 Hz, 1H), 4.65 (d, *J* = 6.4 Hz, 1H), 4.57 (d, *J* = 6.8 Hz, 1H), 3.55 (s, 3H), 3.51-3.54 (m, 1H), 3.35-3.39 (m, 1H), 2.98-3.07 (m, 2H), 2.12 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, d-$CDCl_3$) δ 171.4, 171.4, 140.0, 137.5, 136.6, 136.2, 130.5, 129.5, 129.3, 128.8, 128.5, 128.3, 128.2, 128.2, 127.7, 117.7, 80.6, 72.5, 68.9, 67.3, 53.7, 52.2, 39.9. HRMS (ESI+) calcd. for C29H28N2O2 [M+H] 437.2224, found 437.2215.



8a **13**

To a solution of **12** (33 mg, 0.08 mmol) in acetone (1 ml) was added HCl (1M, 0.4 mmol) dropwised at 0 °C. The reaction mixture was stirred at room temperature for 1 h. The acetone was removed in vacuo and the residue was washed with Et_2O (3 ml) twice. The residue was dried in vacuo to afford the product as a white solid. The free amine was obtained by dissolving the diamine salts in 1 N NaOH solution and extraction with DCM for three times.

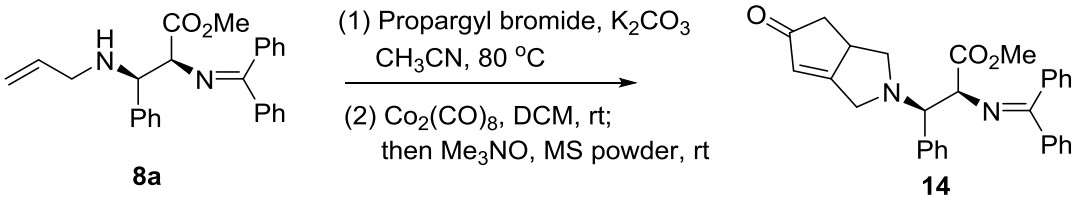
To a solution of free amine (16 mg, 0.07 mmol) in DCM (0.3 ml) was added the $IPrAuNTf_2$ (3 mg, 0.0035 mmol) at rt. The reaction mixture was stirred at rt for 6h. The solvent was removed under vacuum and the residue was purified by flashing chromatography.



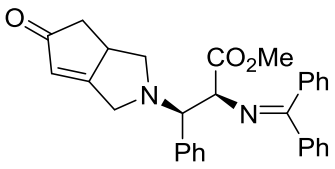
Methyl
(2S,3R)-4-allyl-6-methyl-3-phenyl-1,2,3,4-tetrahydropyrazine-2-carboxylate (13)

Colorless oil, 14 mg, 56% yield over three steps. α_D^{25}= +33 (*c*= 1.0, $CHCl_3$). IR: (neat) 2921, 2852, 1745, 1674, 1643 cm^{-1}; ^{1}H NMR (300 MHz, d-$CDCl_3$) δ 7.36-7.41 (m, 3H), 7.16 (dd, *J* = 7.2, 1.5 Hz, 2H), 5.65-5.78 (m, 1H), 5.23 (d, *J* = 10.2 Hz, 1H), 5.14 (d, *J* =

17.1 Hz, 1H), 5.01 (d, *J* = 2.1 Hz, 1H), 4.85 (d, *J* = 1.5 Hz, 1H), 4.72-4.79 (m, 1H), 3.80 (s, 3H), 3.22 (d, *J* = 8.1 Hz, 1H), 3.17 (d, *J* = 6.9 Hz, 1H), 2.40 (d, *J* = 0.9 Hz, 3H). ^{13}C NMR (125 MHz, d-$CDCl_3$) δ 169.7, 166.5, 156.7, 137.2, 131.8, 129.4, 128.7, 126.6, 119.5, 65.7, 59.2, 53.3, 47.5, 21.8. HRMS (ESI+) calcd. for C16H20N2O2 [M+H] 273.1525, found 273.1530.



To a solution of **12** (33 mg, 0.08 mmol) in DCM (1 ml) was added $Co_2(CO)_8$ (28 mg, 0.08 mmol) at rt. The reaction mixture was stirred at room temperature for 2 h. The starting material was consumed as checked by TLC. To the reaction mixture was added the MS powder (4 Å, 50 mg), followed by Me_3NO (37 mg, 0.5 mmol) at rt. The reaction mixture was vigorously stirred for 6h. The mixture was filtered through a small pad of Celite and washed with DCM (10 ml). The solvent was removed under vacuum and the residue was purified by flashing chromatography.



Methyl (2S,3R)-2-((diphenylmethylene)amino)-3-(5-oxo-3,3a,4,5-tetrahy drocyclopenta[c]pyrrol-2(1H)-yl)-3-phenylpropanoate (14)

Colorless oil, 30 mg, 65% yield over two steps. α_D^{25}= -72.1 (*c*= 1.0, $CHCl_3$). IR: (neat) 2920, 1738, 1709, 1627, 1236 cm^{-1}; dr =1:1, ^{1}H NMR (500 MHz, d-$CDCl_3$) δ 7.87-7.89 (m, 4H), 7.61-7.65 (m, 5H), 7.56-7.59 (m, 5H), 7.51-7.54 (m, 2H), 7.46-7.48 (m, 8H), 7.40-7.42 (m, 2H), 7.21-7.22 (m, 2H), 6.99-7.01 (m, 2H), 6.07 (s, 1H), 6.02 (s, 1H), 4.82 (d, *J* = 6.5 Hz, 1H), 4.68 (s, 2H), 4.65 (d, *J* = 7.0 Hz, 1H), 4.35 (d, *J* = 12.5 Hz, 1H), 3.90-3.95 (m, 2H), 3.81 (s, 3H), 3.73 (s, 3H), 3.65 (d, *J* = 12.5 Hz, 1H), 3.46-3.50 (m, 1H), 3.33-3.37 (m, 1H), 3.28-3.30 (m, 1H), 3.25-3.26 (m, 1H), 2.76-2.81 (m, 1H),

2.67-2.72 (m, 1H), 2.42-2.45 (m, 1H), 2.26-2.32 (m, 1H), 2.16-2.20 (m, 1H), 2.07-2.11 (m, 1H). ^{13}C NMR (125 MHz, d-$CDCl_3$) δ 210.0, 209.9, 186.9, 186.8, 171.8, 171.6, 171.5, 171.3, 139.8, 138.6, 137.6, 136.1, 136.1, 130.8, 130.7, 130.3, 129.3, 129.2, 129.2, 129.0, 128.9, 128.8, 128.6, 128.5, 128.5, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 124.3, 124.2, 70.4, 70.0, 69.9, 69.8, 56.1, 55.2, 52.4, 52.2, 51.9, 51.5, 46.0, 45.6, 40.5, 40.3. HRMS (ESI+) calcd. for C30H28N2O3 [M+H] 465.2173, found 465, 2164.

VIII. References:

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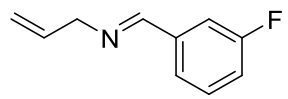
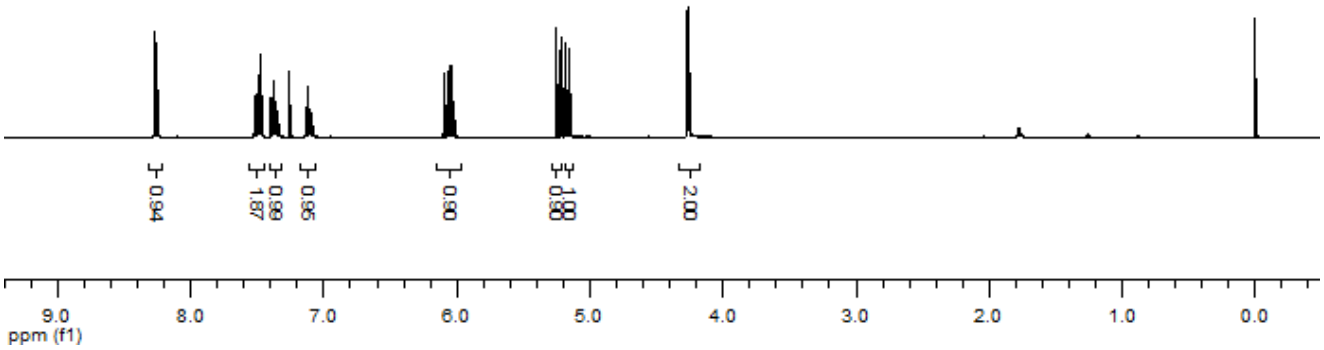
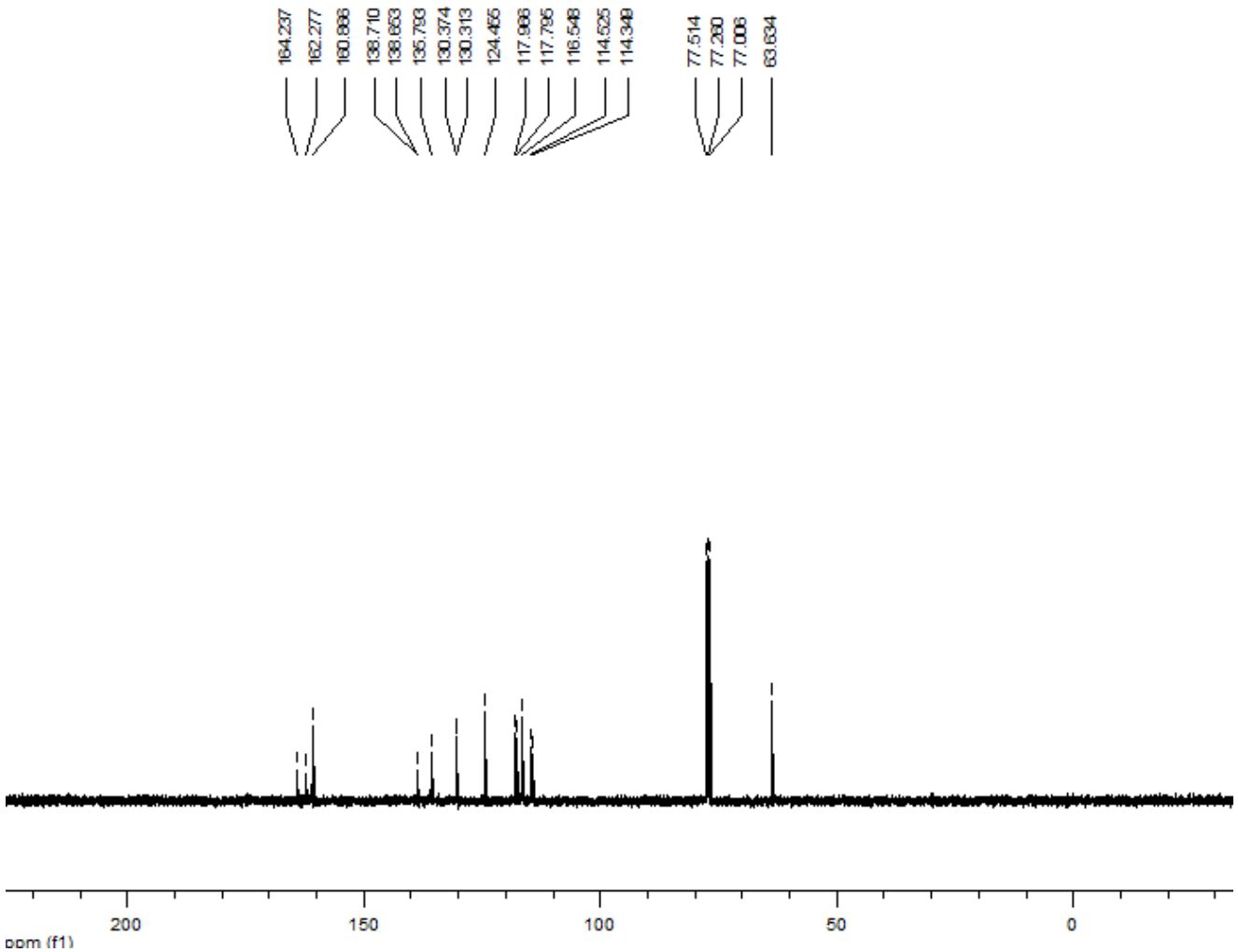
5. Arai, T.; Mishiro, A.; Matsumura, E.; Awata, A.; Shirasugi, M. *Chem. Eur. J.* **2012**, *18*, 11219.



1i

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160.866
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135.793
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130.313
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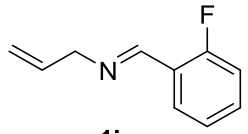
117.966
117.795
116.548
114.525
114.349
77.514
77.200
77.006
63.634
200
150
100
50
0
ppm (f1)



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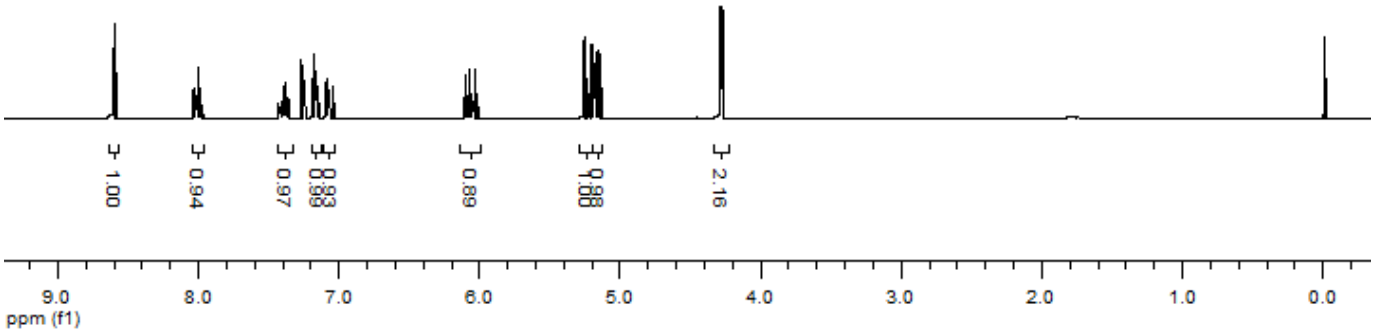

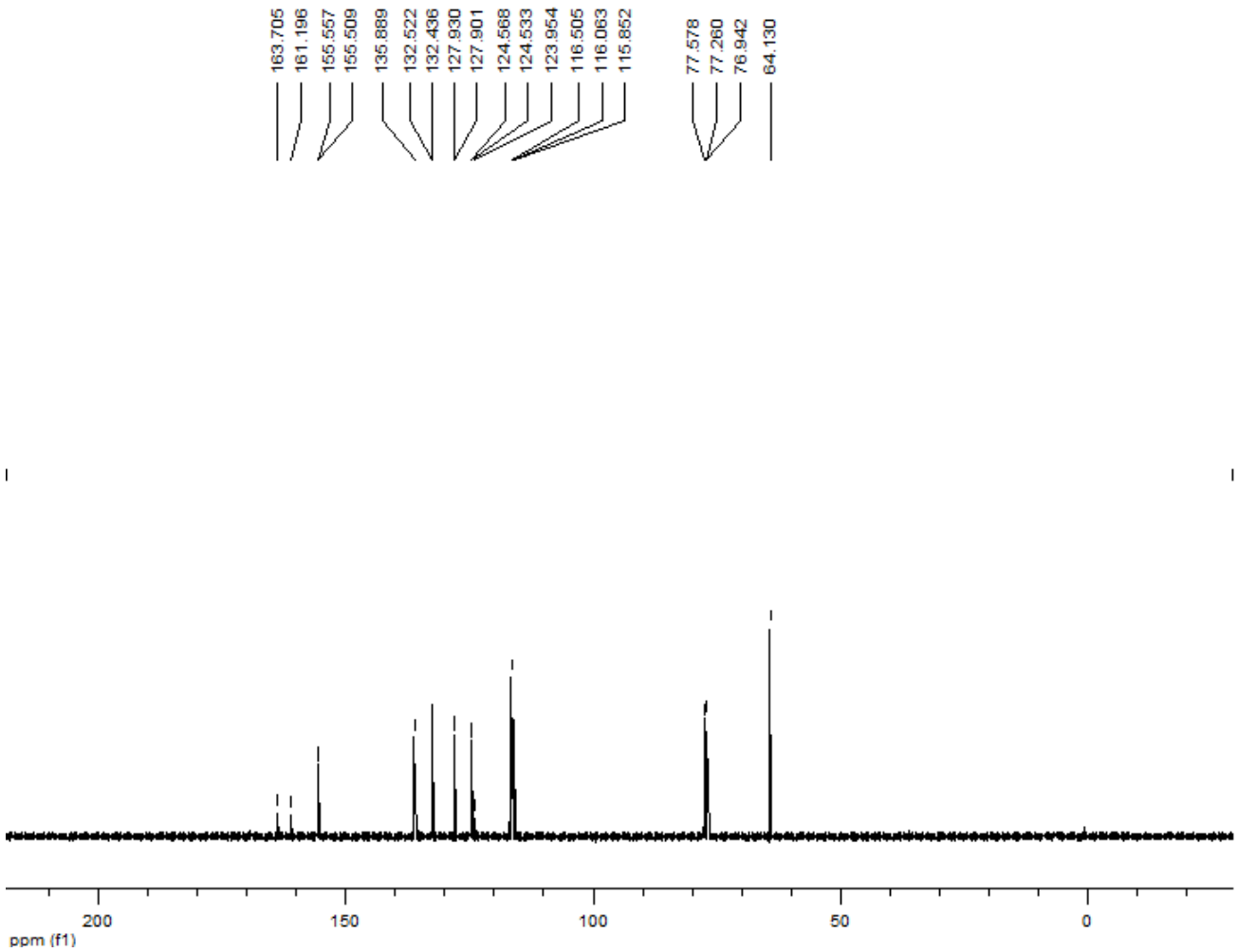
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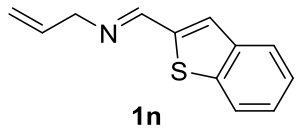
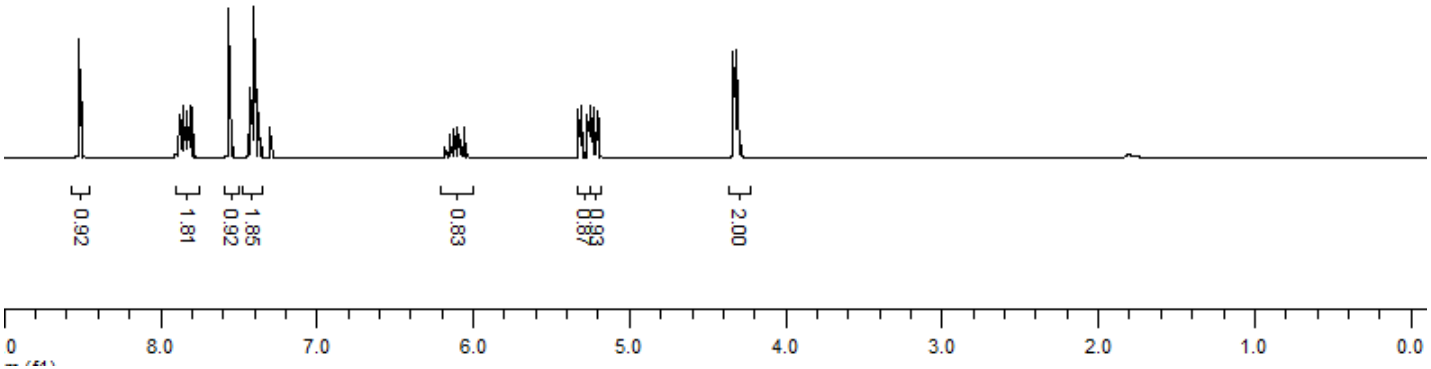
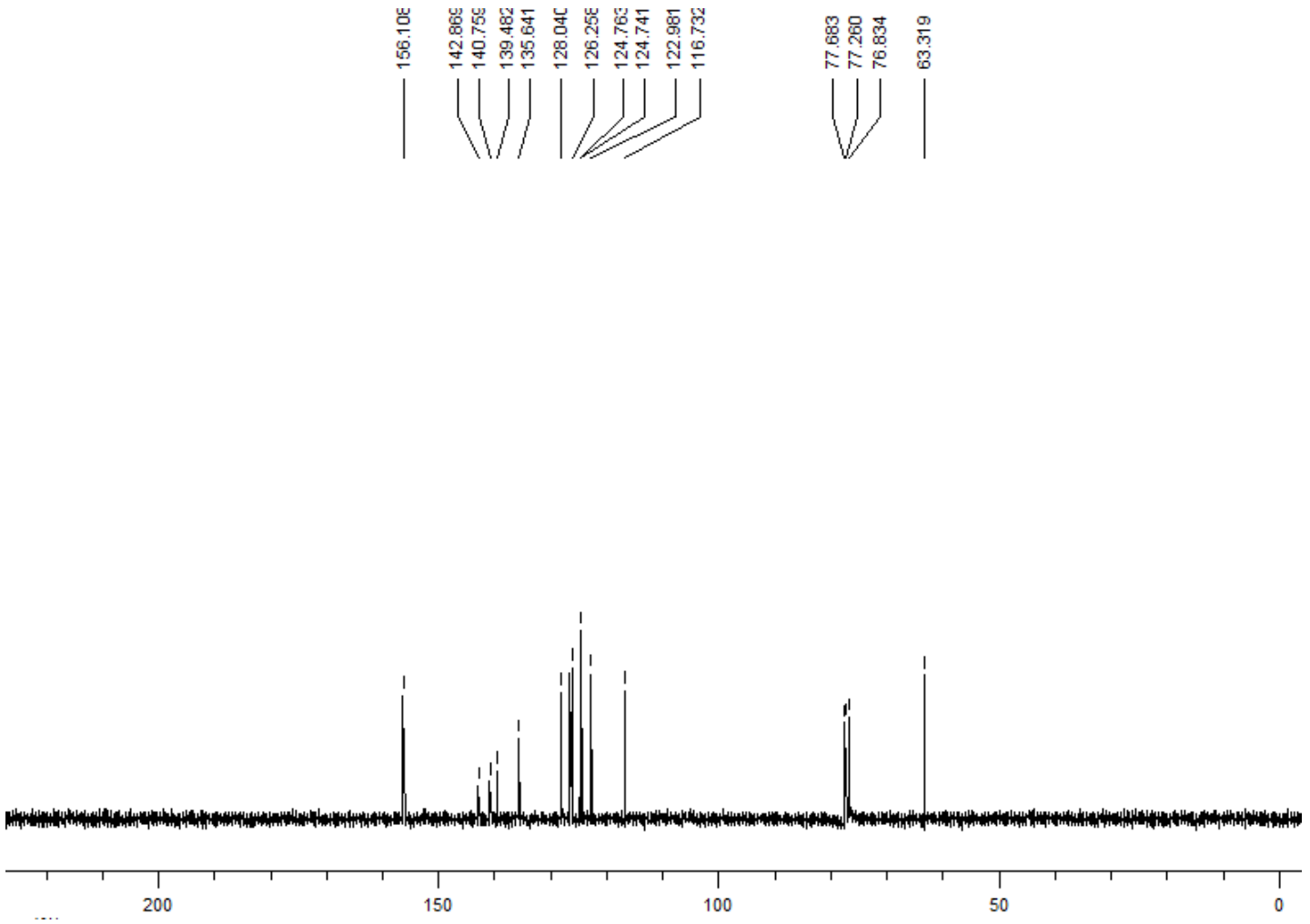
161.196
155.557
155.509
135.889
132.522
132.436
127.930
127.901
124.568
124.533
123.954
116.505
116.063
115.852
77.578
77.260
76.942
64.130
200
150
100
50
0
ppm (f1)



1n

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139.482
135.641
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124.763
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122.981
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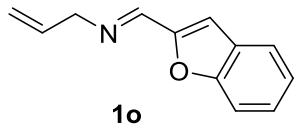
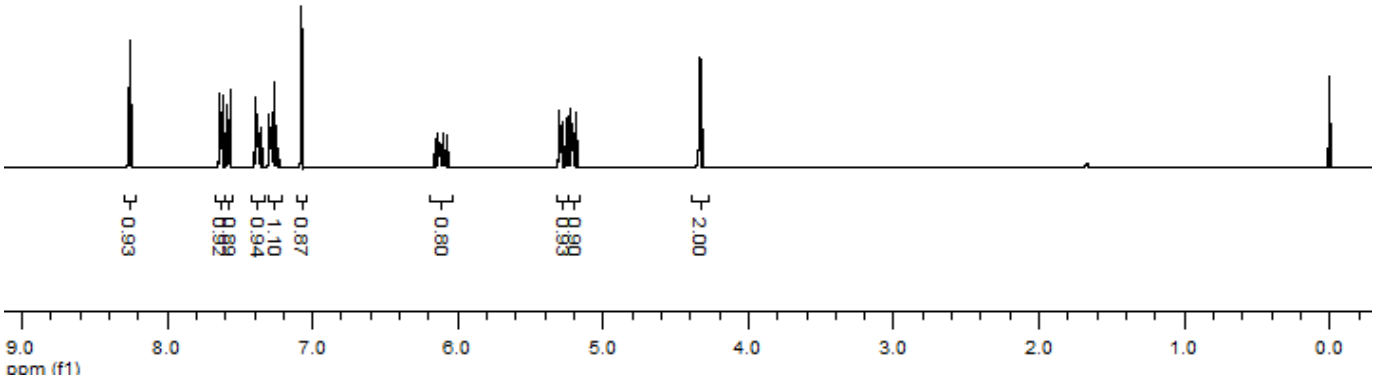
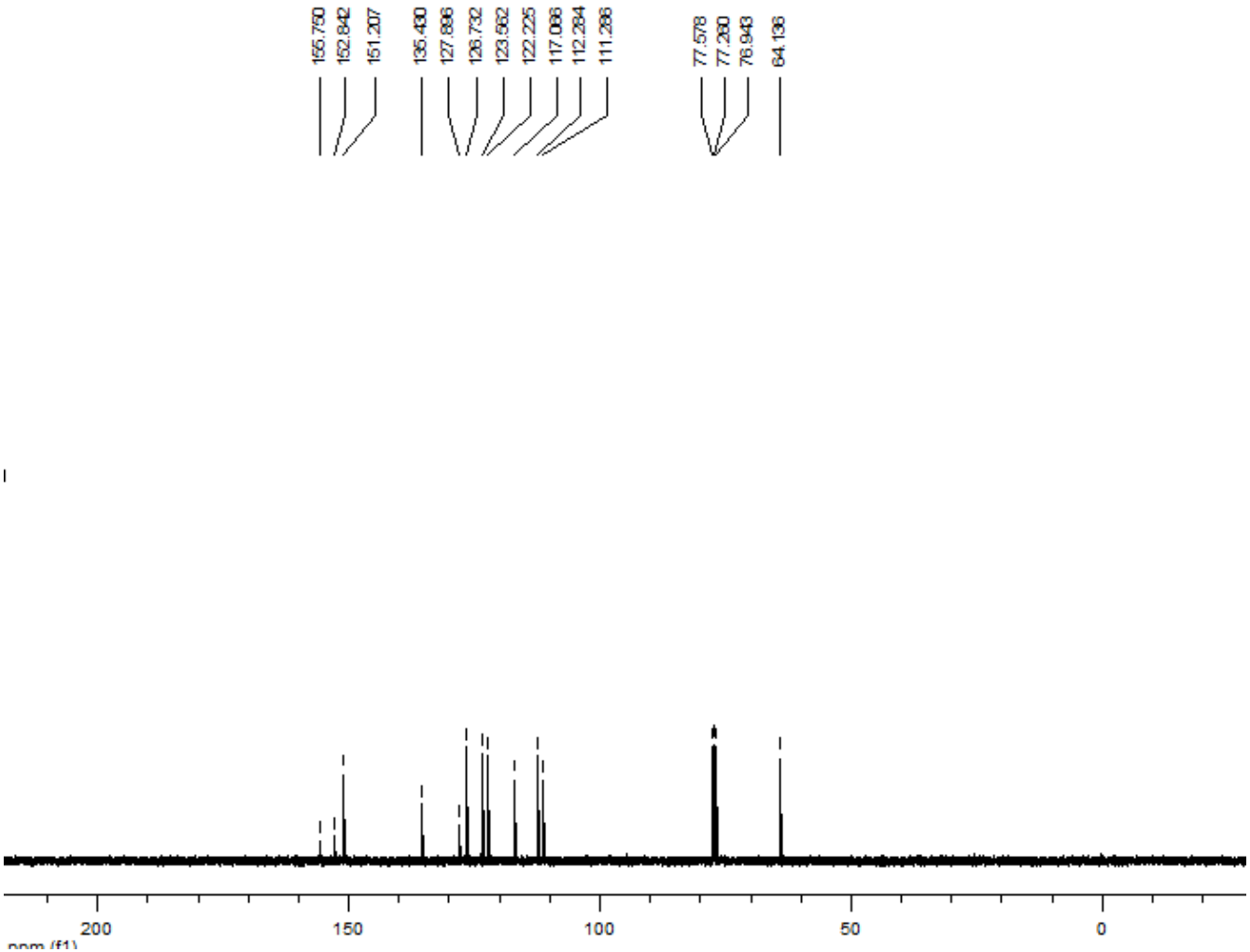
77.260
76.834
63.319
200
150
100
50
0



1o

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111.286
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77.260
76.943
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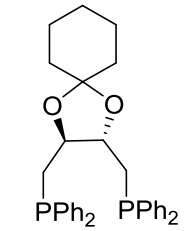
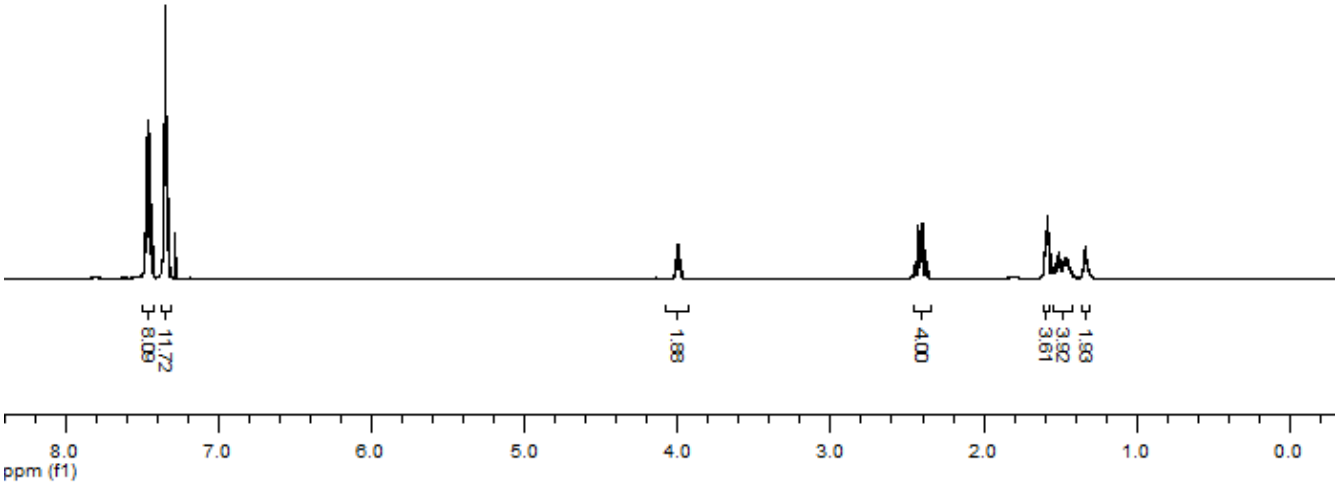
200
150
100
50
0
ppm (f1)


O
O
PPh2
PPh2

(S,S)-Cy DIOP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3.61
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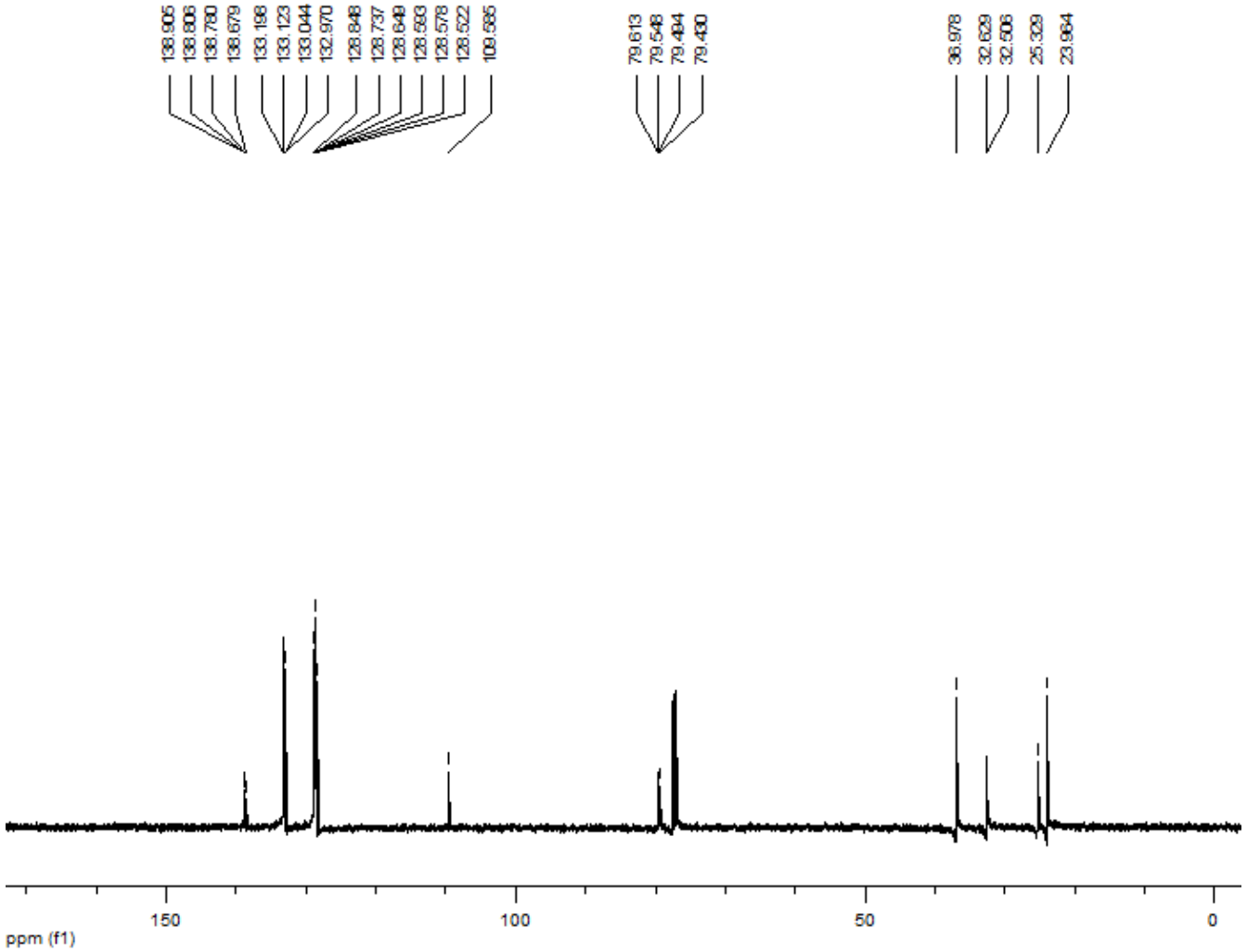
1.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)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128.578
128.522
109.585
79.613
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100
50
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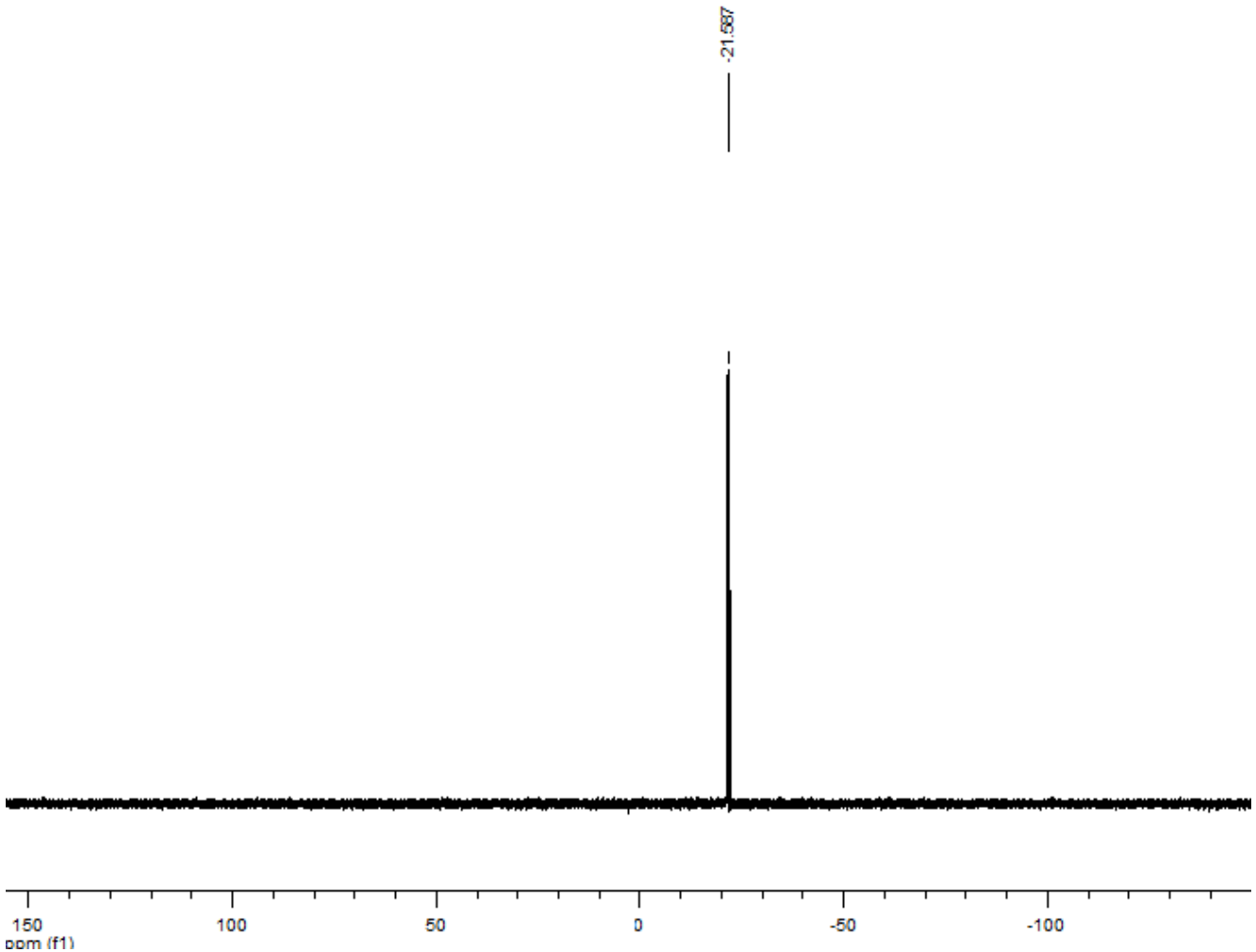
ppm (f1)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100
50
0
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-100
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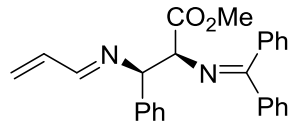
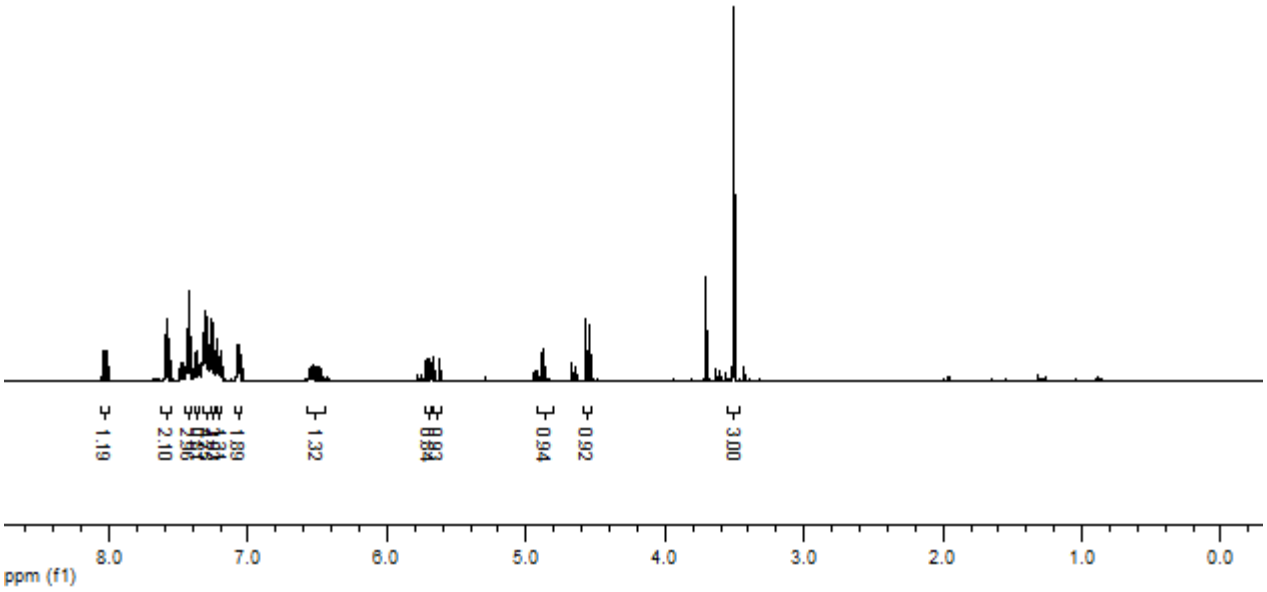

CO2Me
Ph
N
N
Ph
Ph

3b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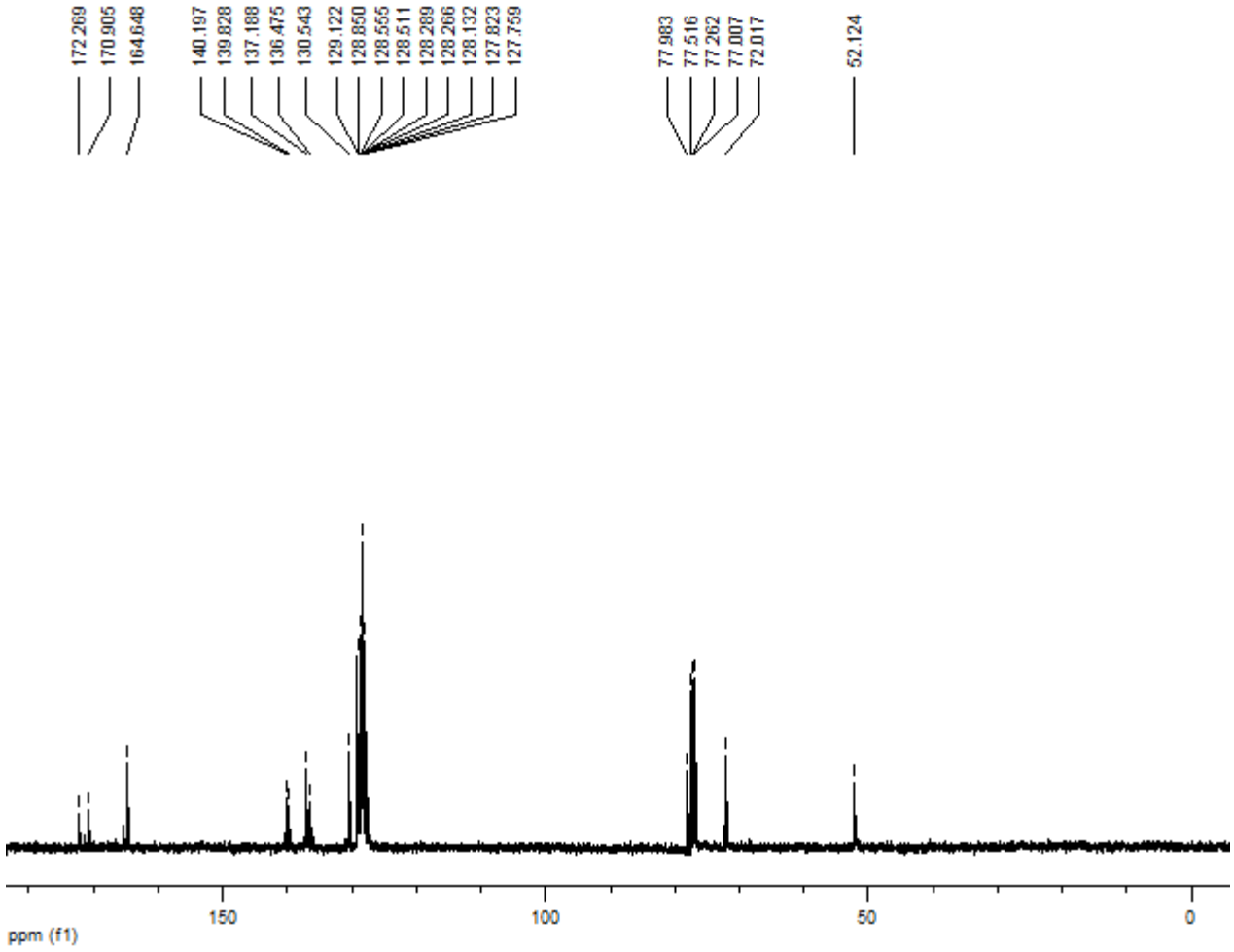
4.0
3.0
2.0
1.0
0.0
ppm (f1)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130.543
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128.289
128.266
128.132
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77.262
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150
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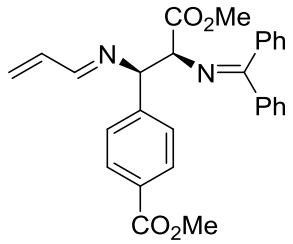
50
0
ppm (f1)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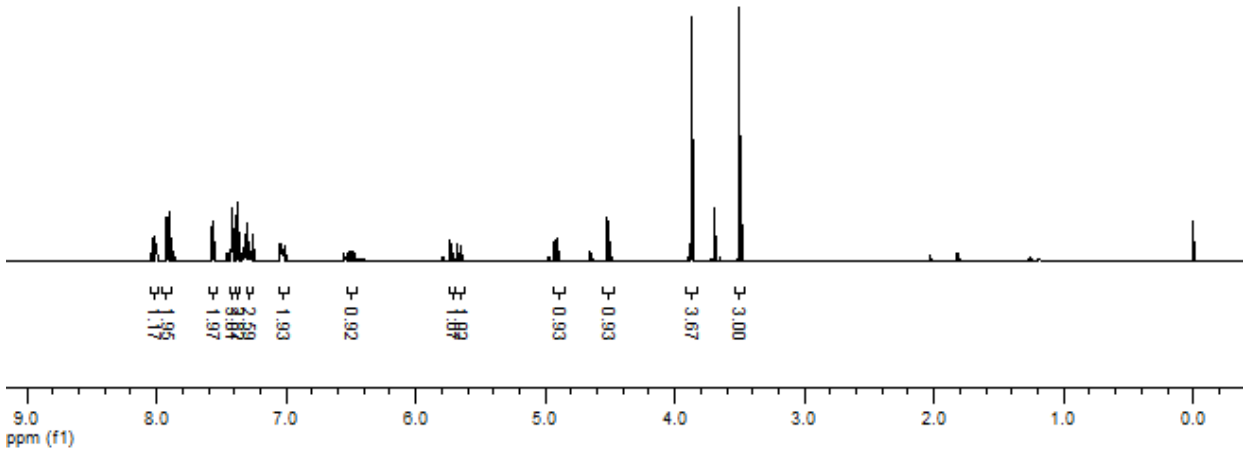
N
N
Ph
Ph
CO2Me

3c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2.61
2.62
2.63
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0.93
0.93
3.67
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1.0
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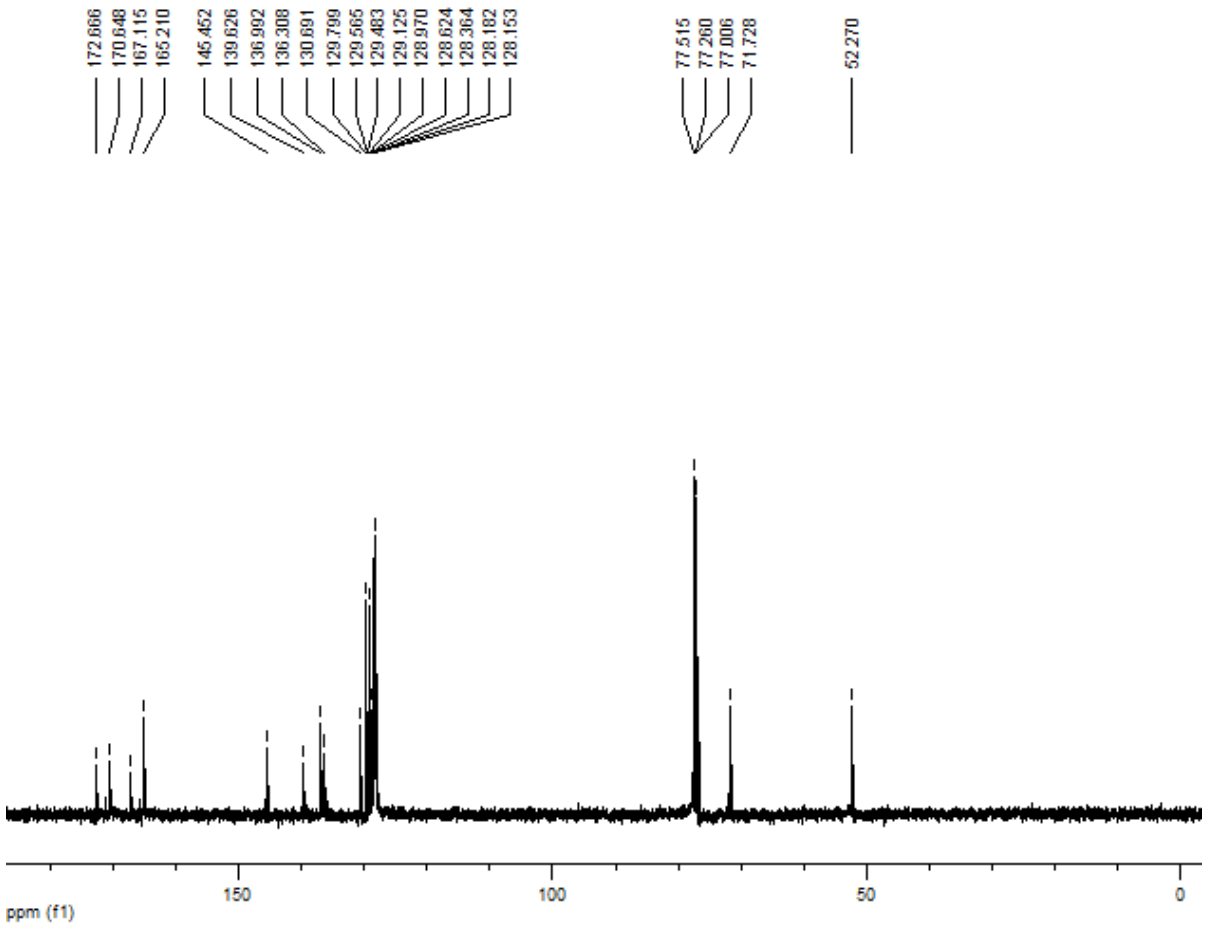
ppm (f1)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136.308
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129.799
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129.483
129.125
128.970
128.624
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128.153
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77.260
77.006
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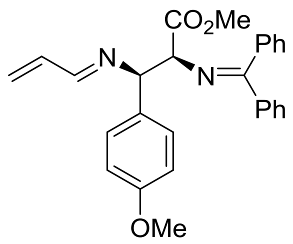
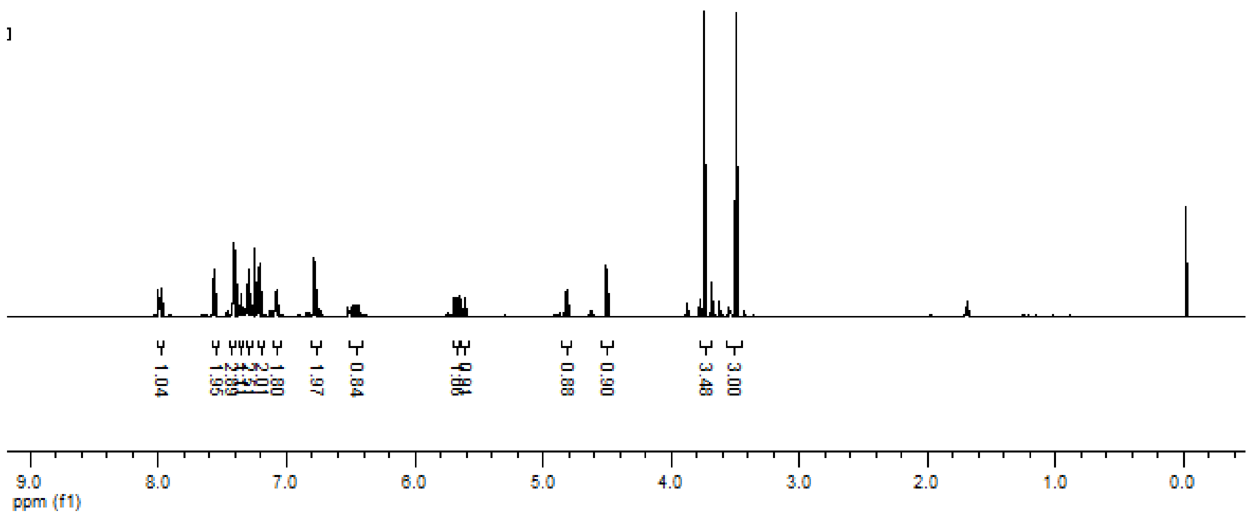
150
100
50
0
ppm (f1)


CO2Me
Ph
N
N
Ph
OMe

3d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1.97
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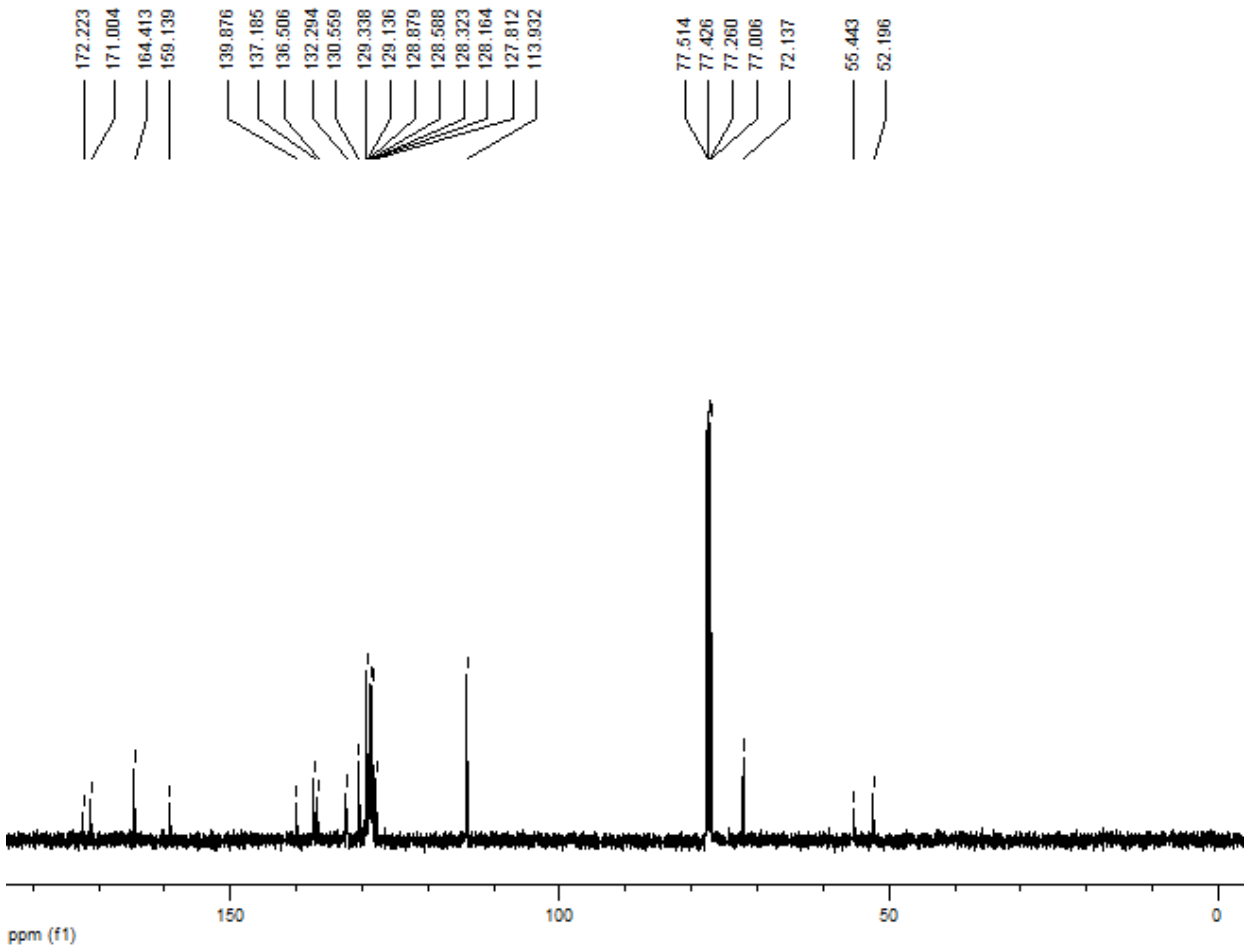
ppm (f1)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128.164
127.812
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77.426
77.260
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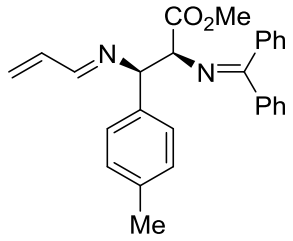
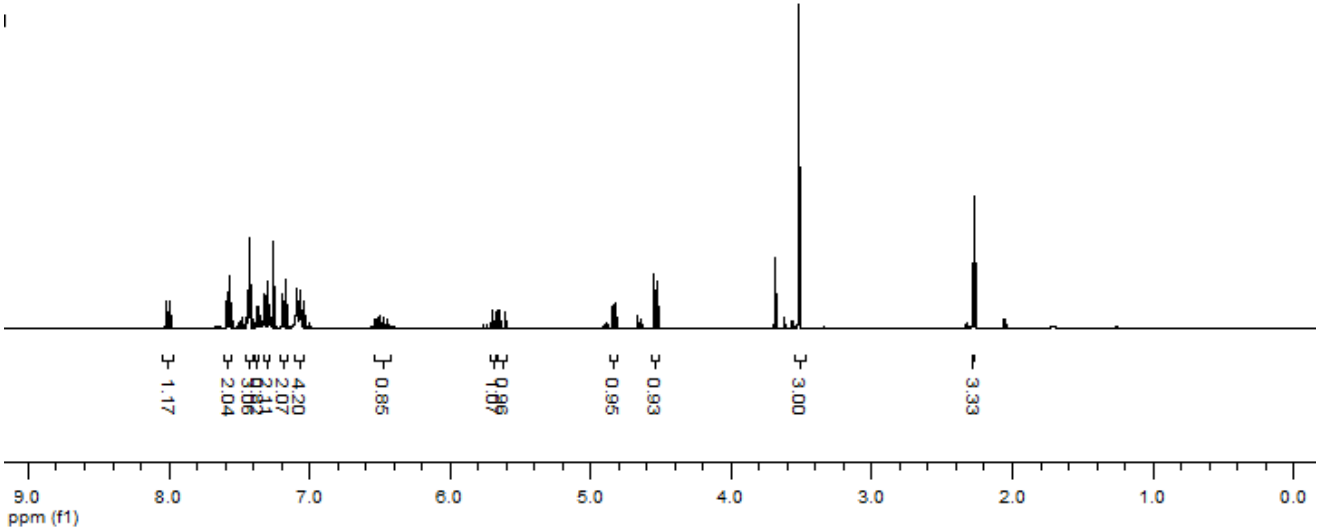
100
50
0
ppm (f1)


CO2Me
Ph
N
N
Ph
Me

3e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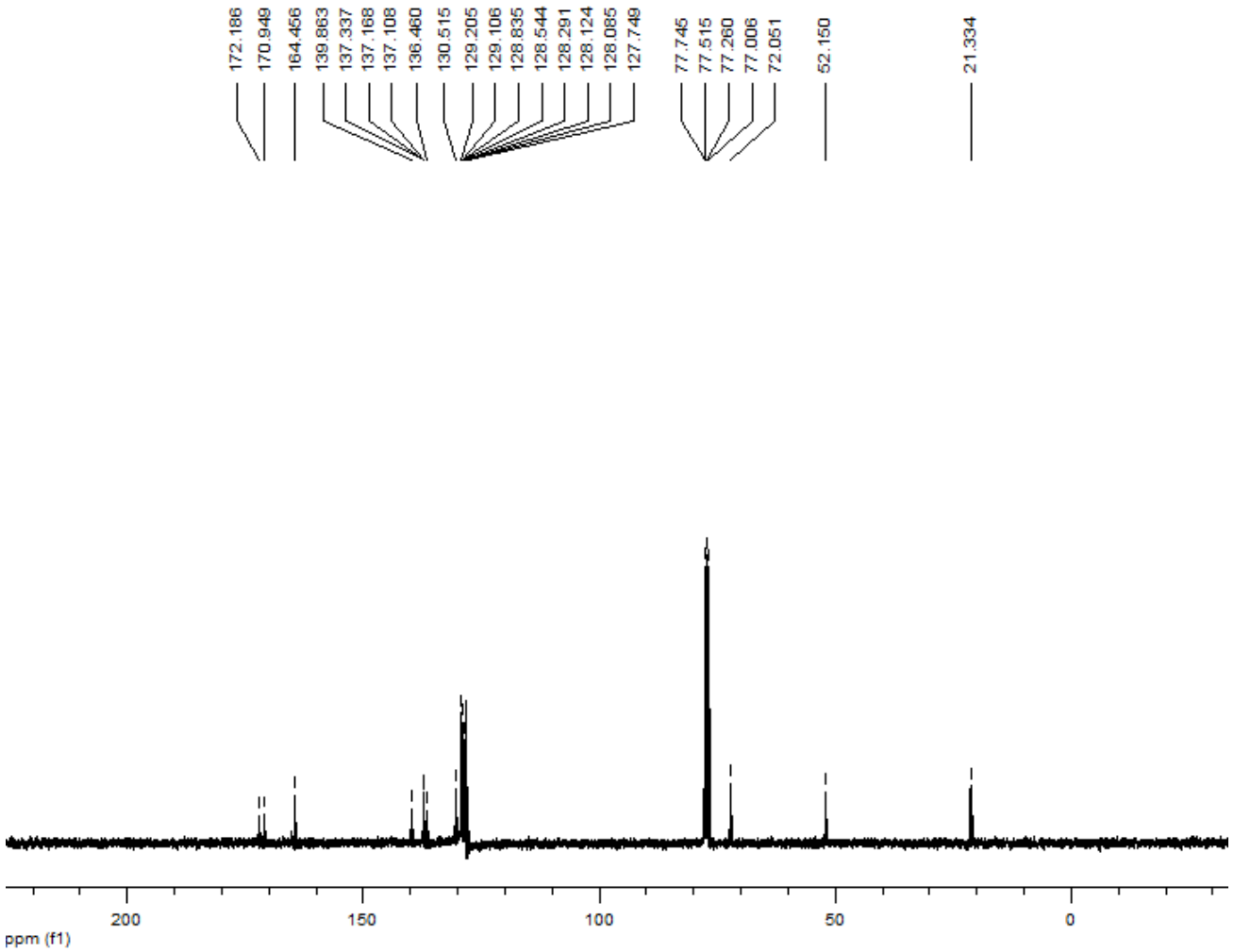
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128.085
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50
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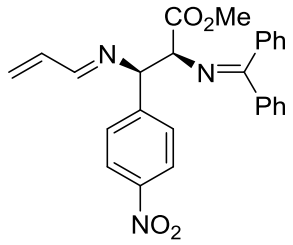
ppm (f1)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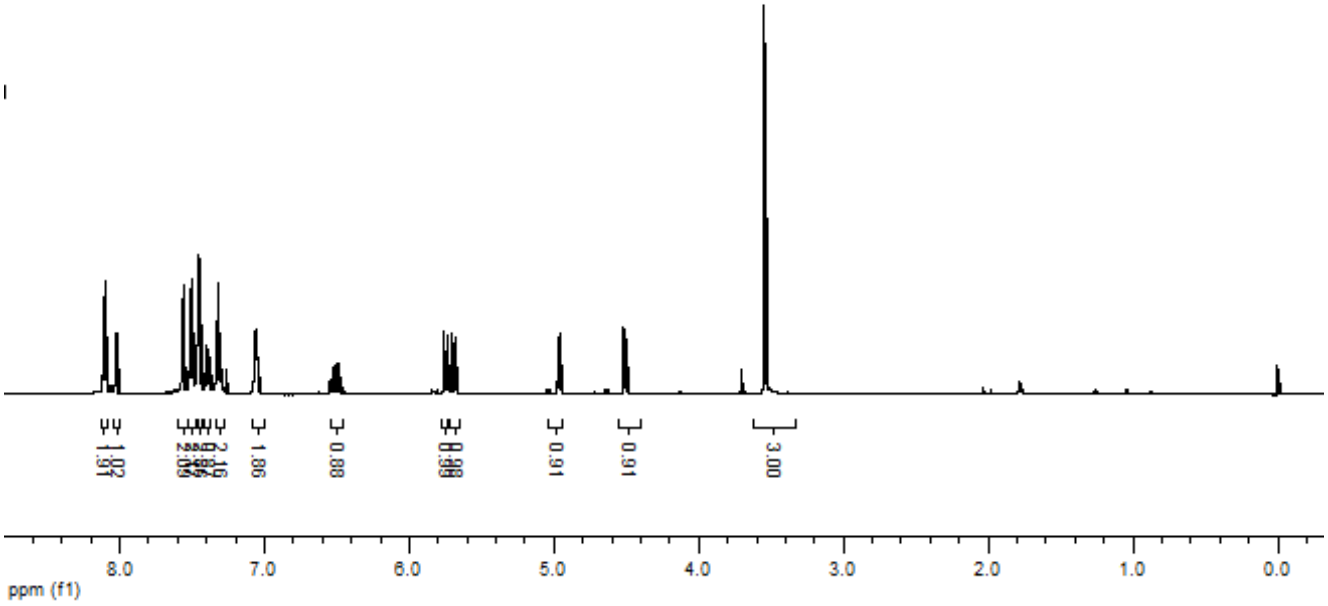
Ph
N
N
Ph
NO2

3f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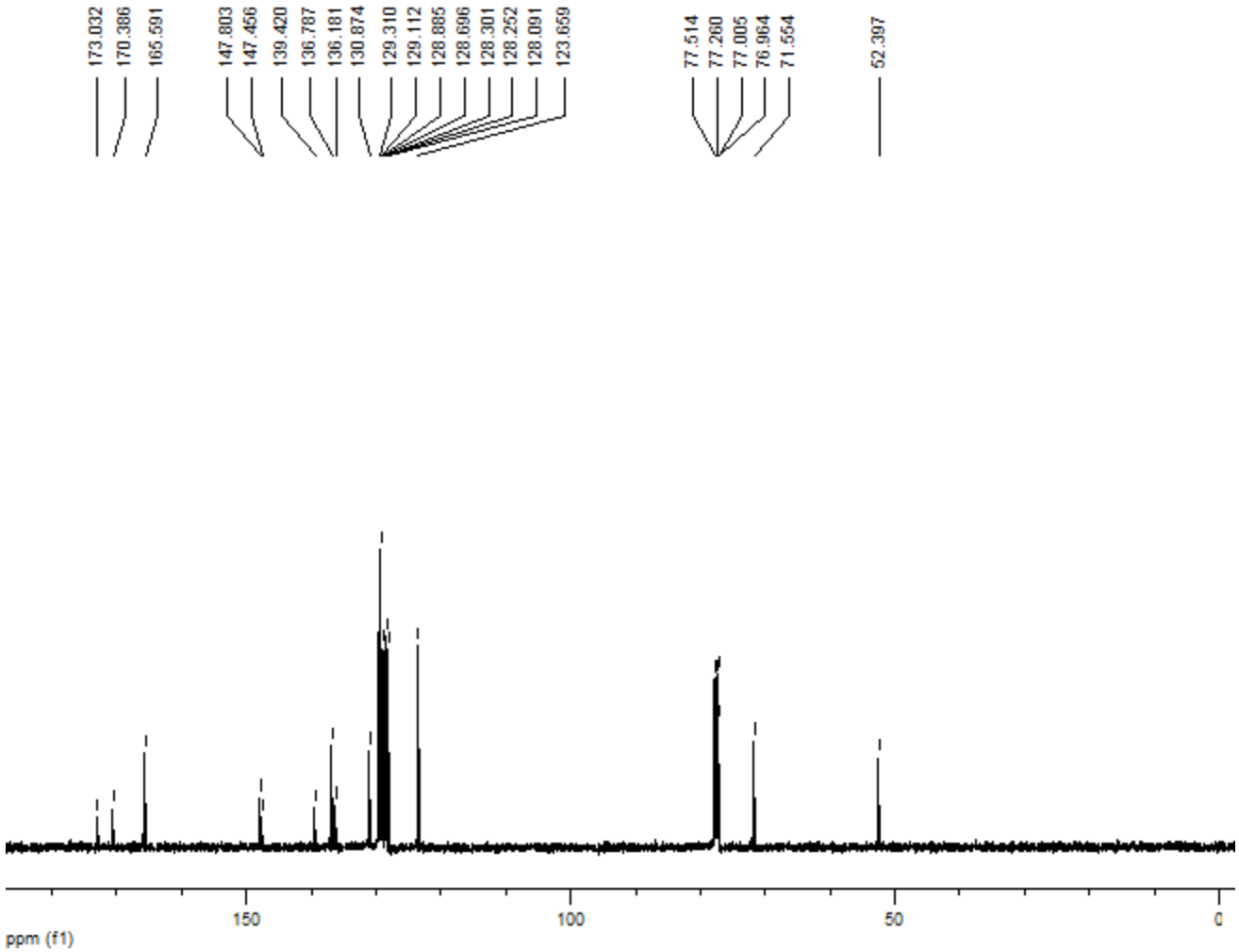
ppm (f1)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128.301
128.252
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50
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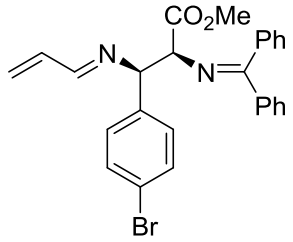
ppm (f1)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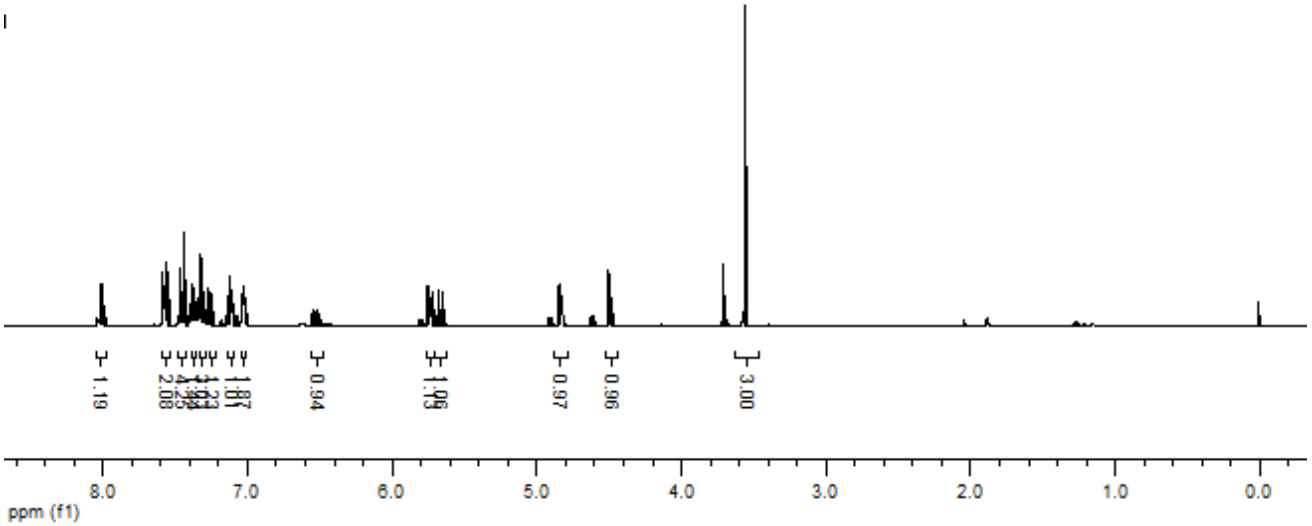
N
Ph
Br

3g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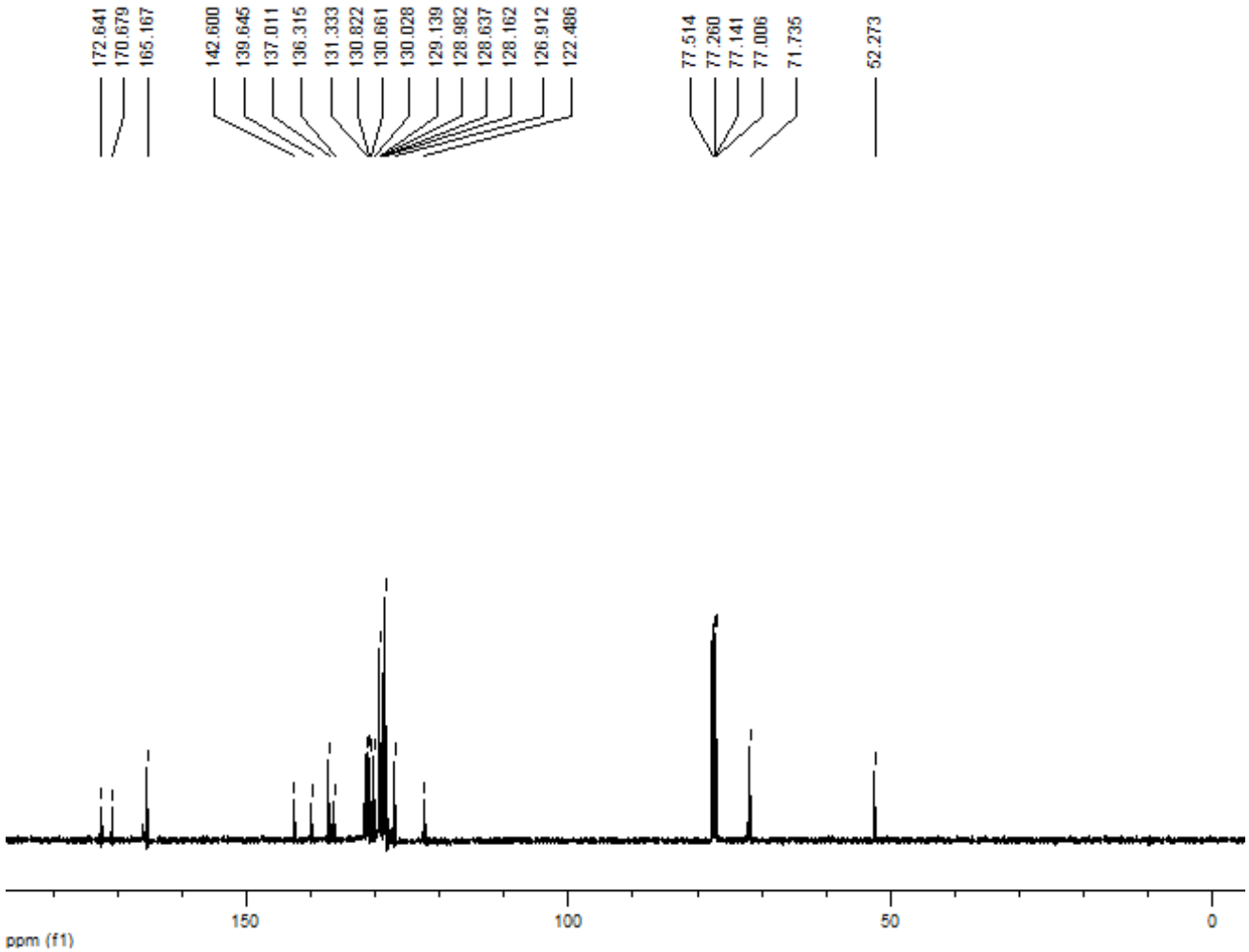
ppm (f1)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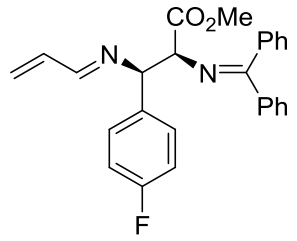
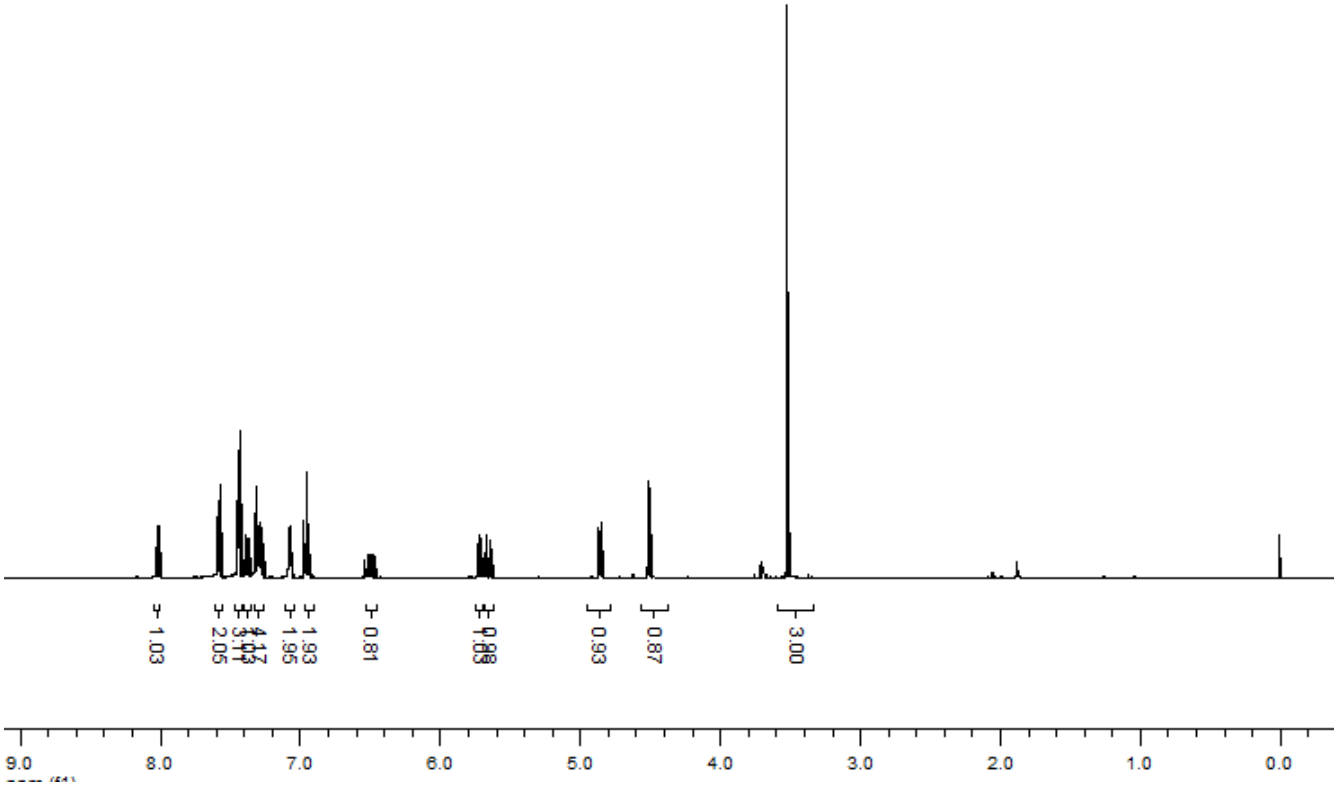
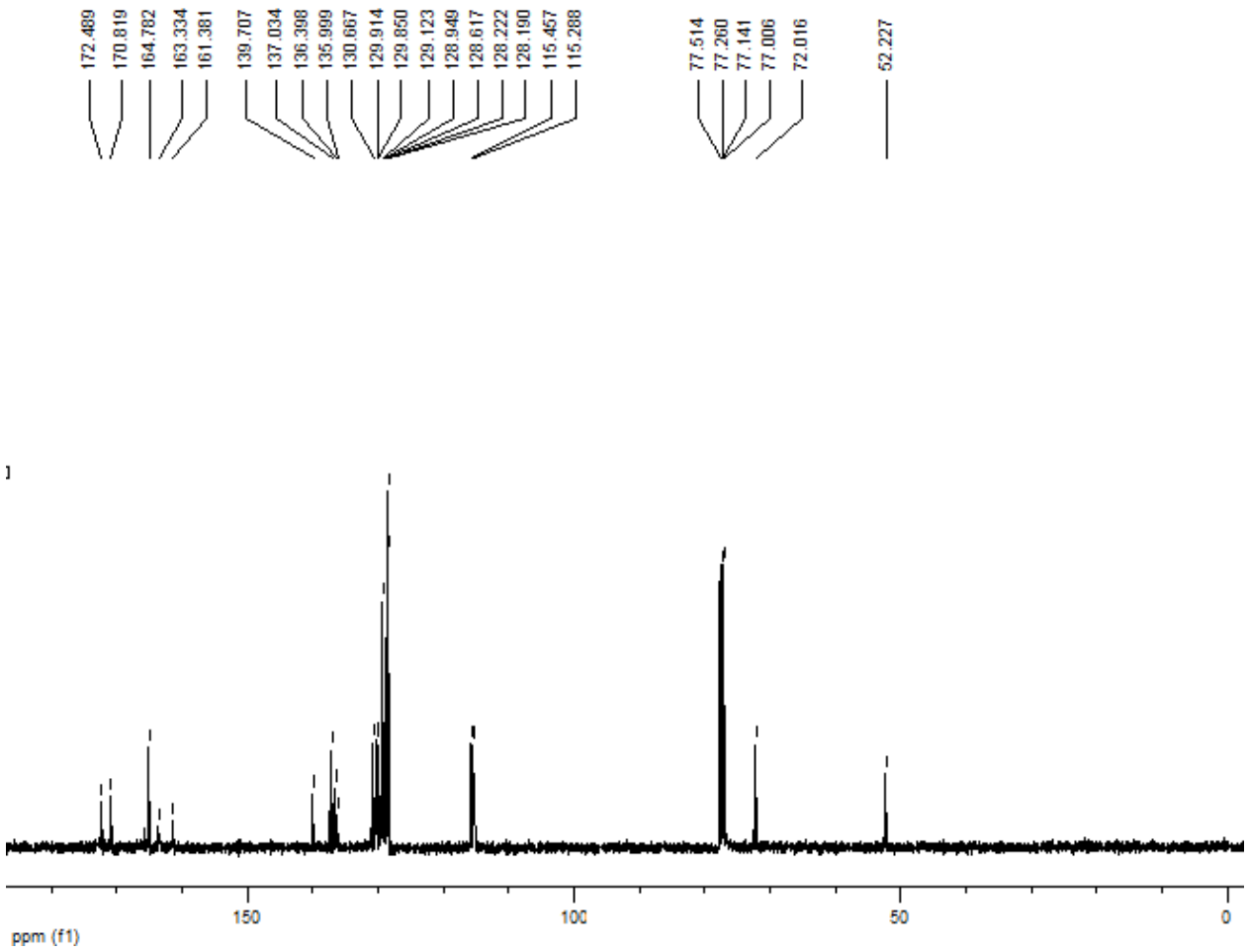
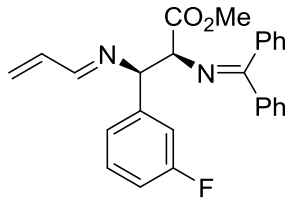
128.637
128.162
126.912
122.486
77.514
77.260
77.141
77.006
71.735
52.273
150
100
50
0
ppm (f1)


CO2Me
Ph
N
N
Ph
F

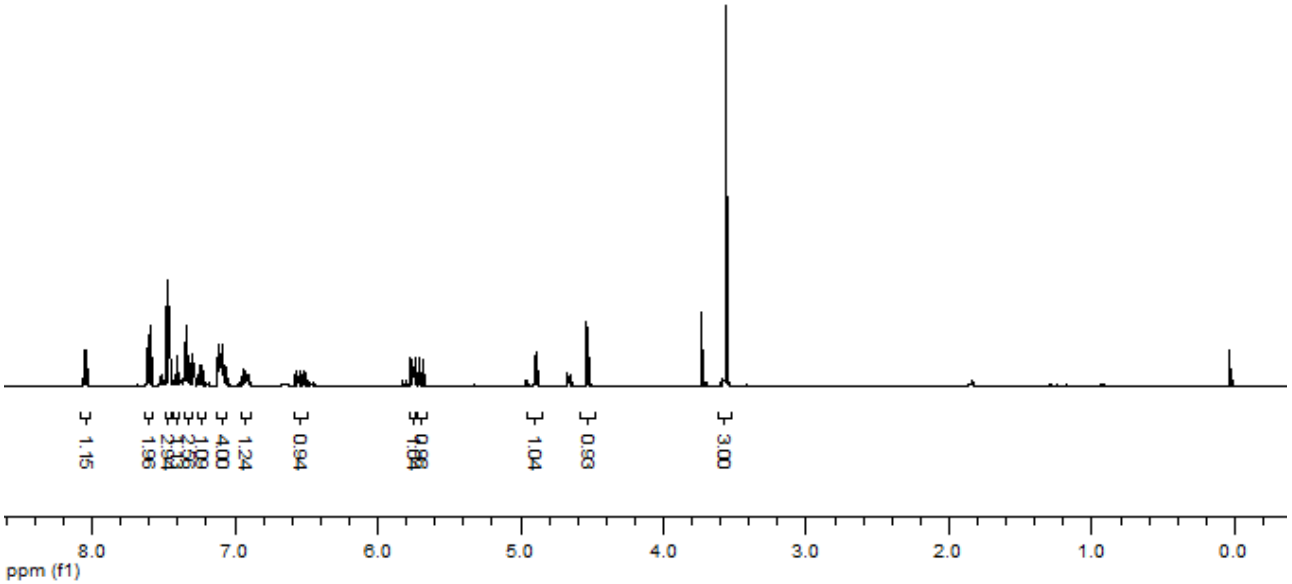
3h

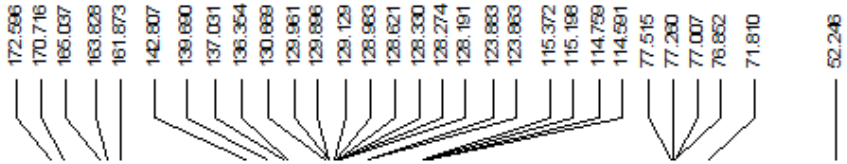

1.03
2.05
1.95
1.93
0.81
0.93
0.87
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

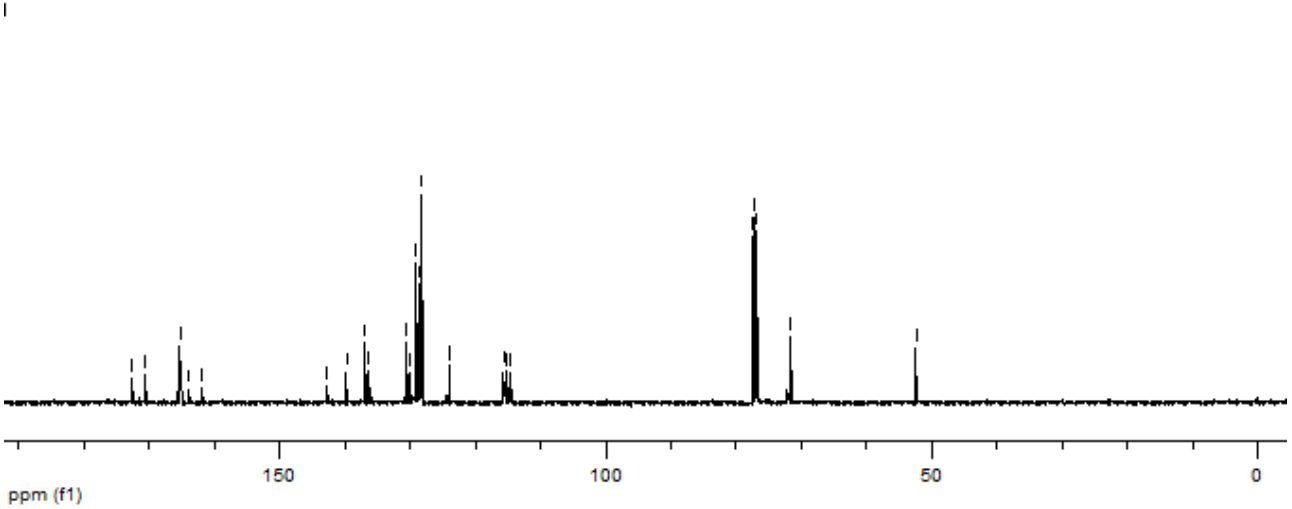

172.489
170.819
164.782
163.334
161.381
139.707
137.034
136.398
135.999
130.667
129.914
129.850
129.123
128.949
128.617
128.222
128.190
115.457
115.288
77.514
77.260
77.141
77.006
72.016
52.227
150
100
50
0
ppm (f1)

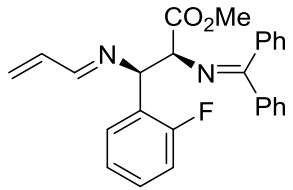

CO2Me
Ph
N
N
Ph
F

3i

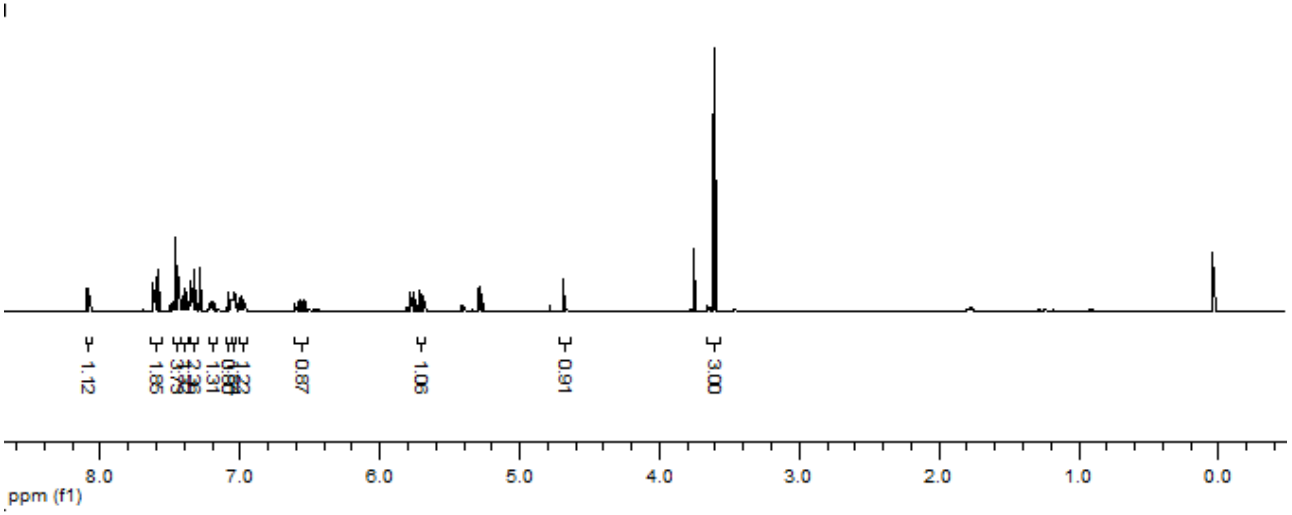

1.15
1.96
4.00
1.24
0.94
1.04
0.93
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

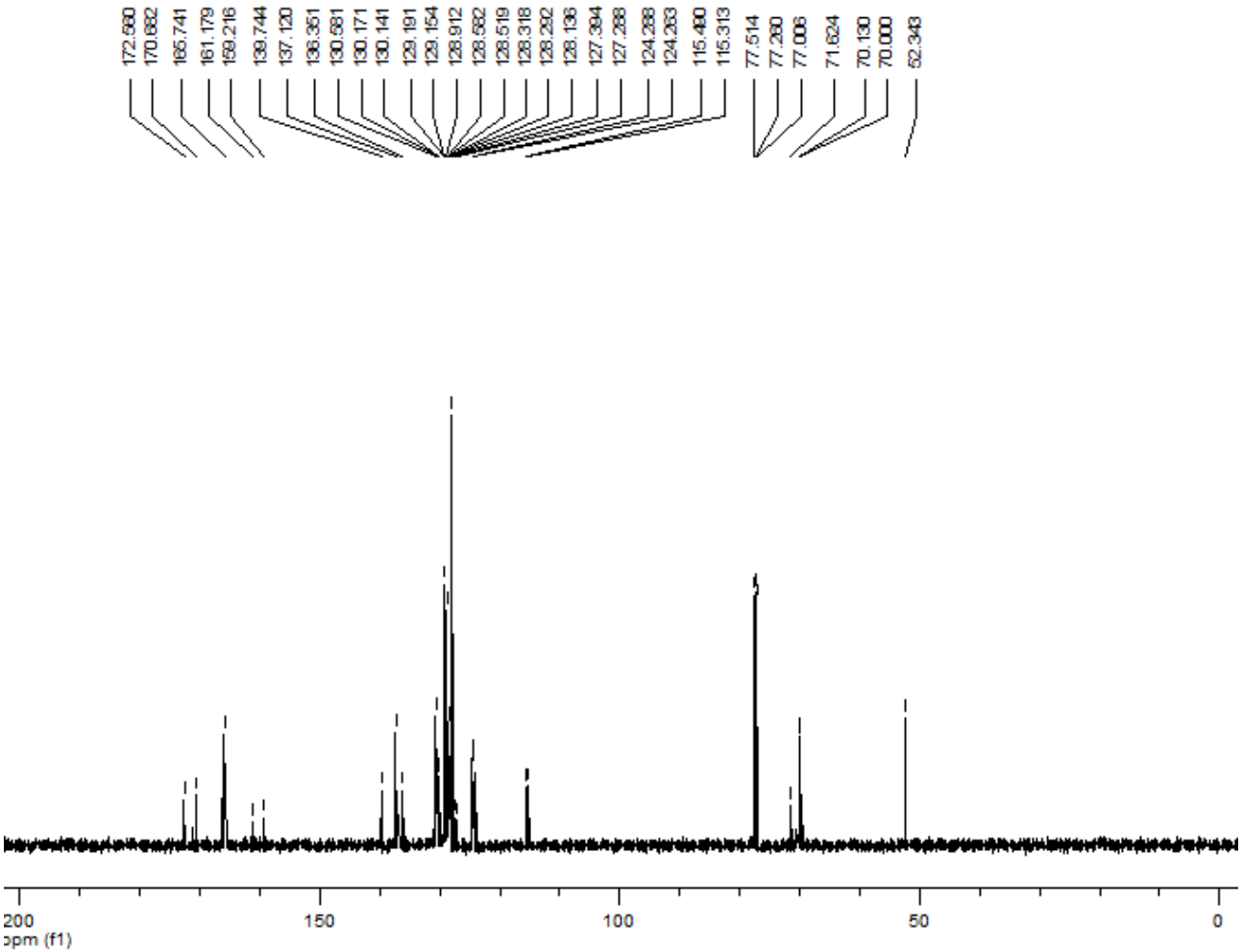

172.596
170.716
165.037
163.628
161.873
142.607
139.690
137.031
136.354
130.669
129.961
129.896
129.129
128.963
128.621
128.330
128.274
128.191
123.883
123.863
115.372
115.198
114.759
114.591
77.515
77.260
77.007
76.852
71.810
52.246

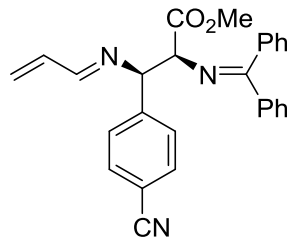

150
100
50
0
ppm (f1)


CO2Me
Ph
N
N
Ph
F

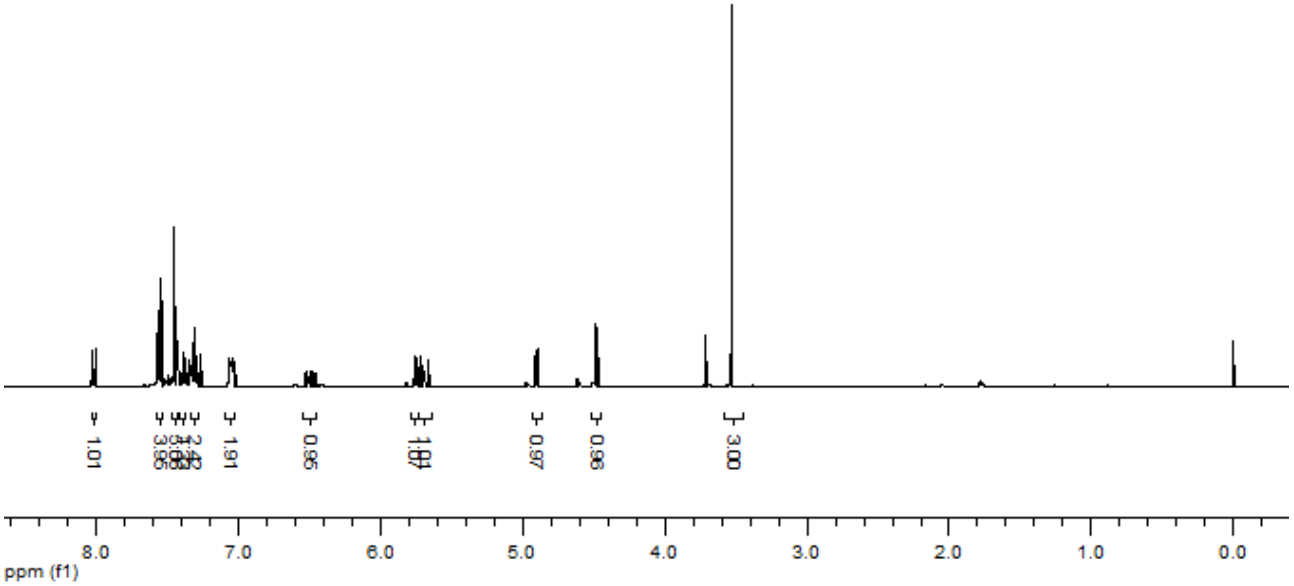
3j

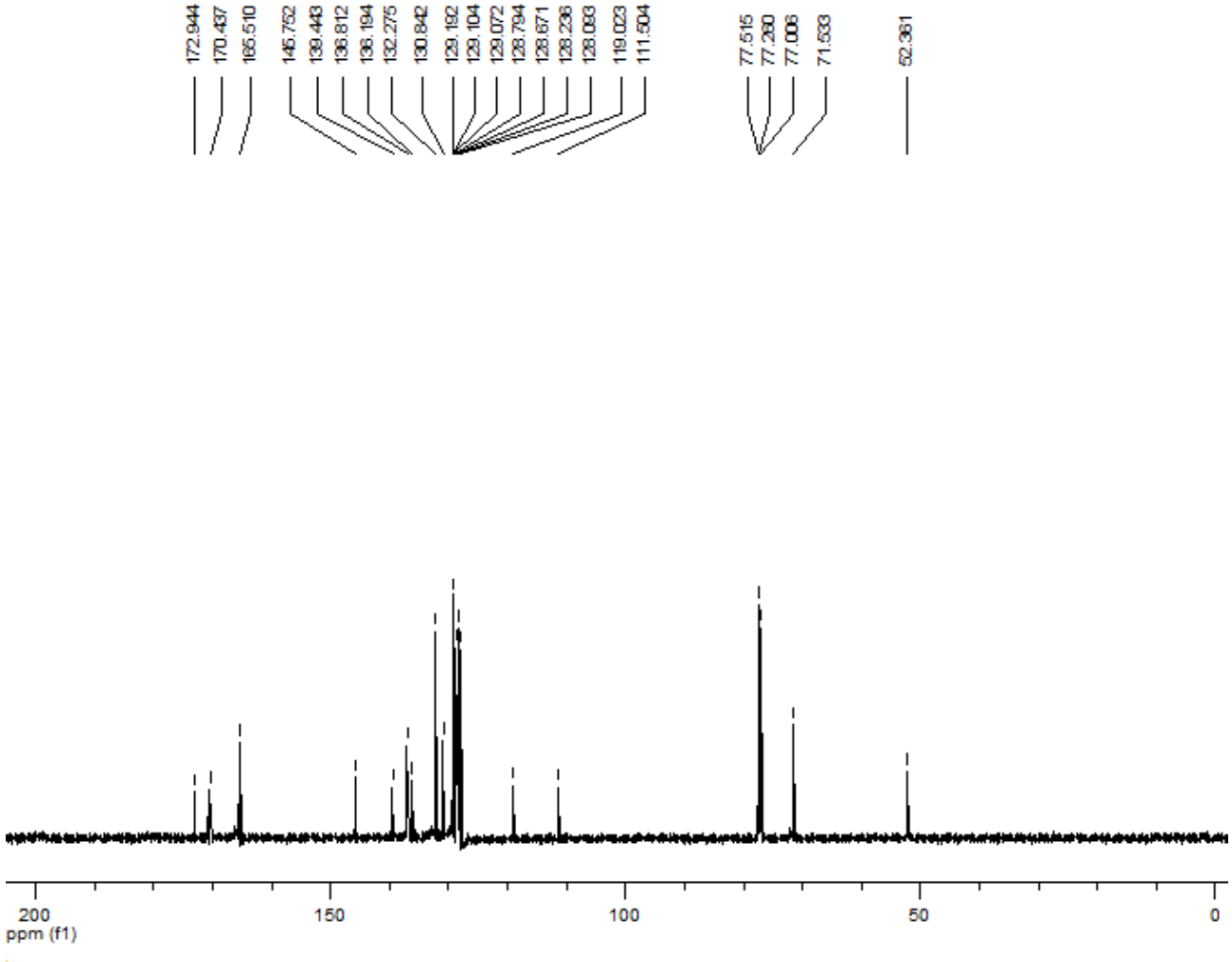

1.12
1.85
1.31
0.87
1.06
0.91
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

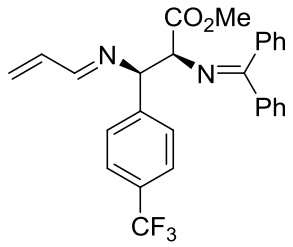

172.680
170.882
165.741
161.179
159.216
139.744
137.120
136.351
130.581
130.171
130.141
129.191
129.154
128.912
128.682
128.519
128.318
128.292
128.136
127.394
127.288
124.288
124.283
115.480
115.313
77.514
77.200
77.006
71.624
70.130
70.000
52.343
200
150
100
50
0
ppm (f1)


CO2Me
Ph
N
N
Ph
CN

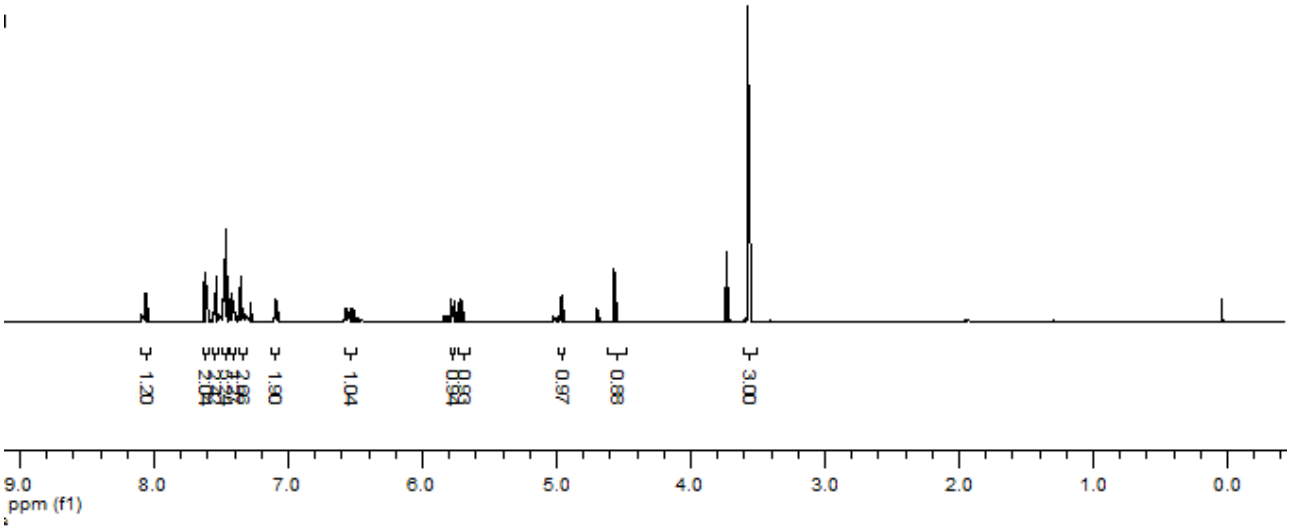
3k

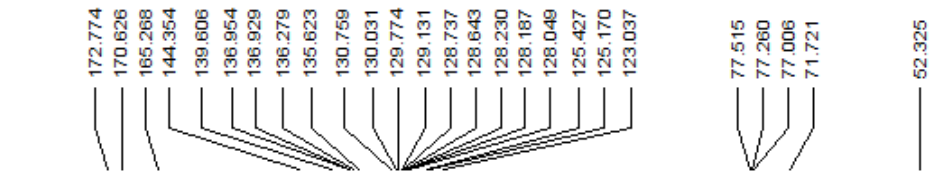

1.01
1.91
0.95
0.97
0.96
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

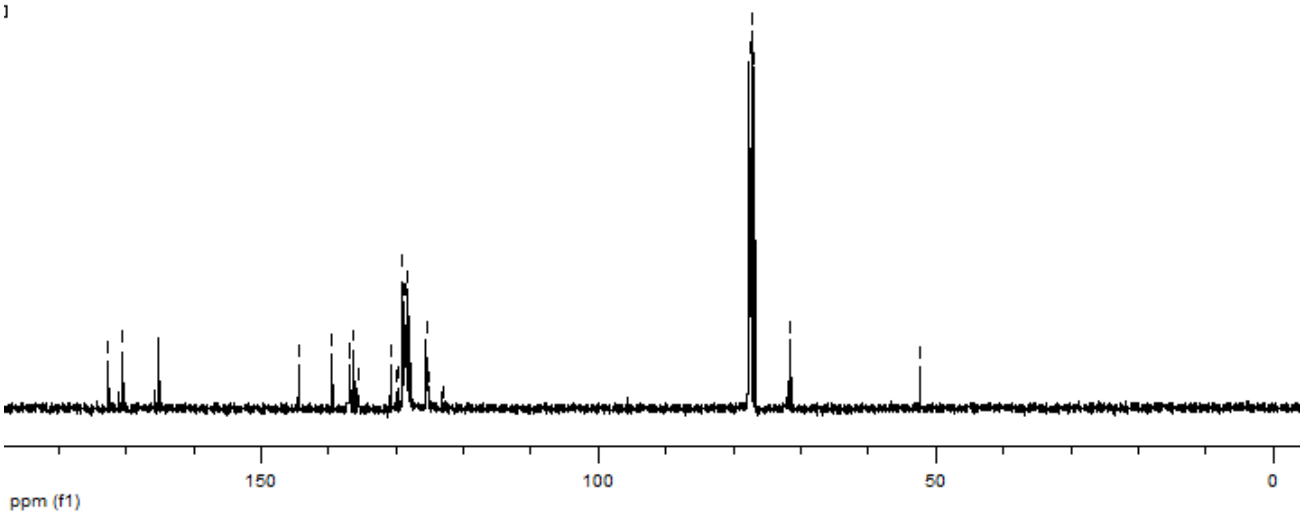

172.944
170.437
165.510
145.752
139.443
136.812
136.194
132.275
130.842
129.192
129.104
129.072
128.794
128.671
128.236
128.053
119.023
111.504
77.515
77.260
77.006
71.533
52.361
200
150
100
50
0
ppm (f1)

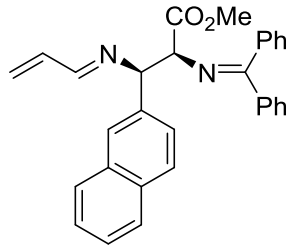

CO2Me
Ph
N
N
Ph
CF3

3l

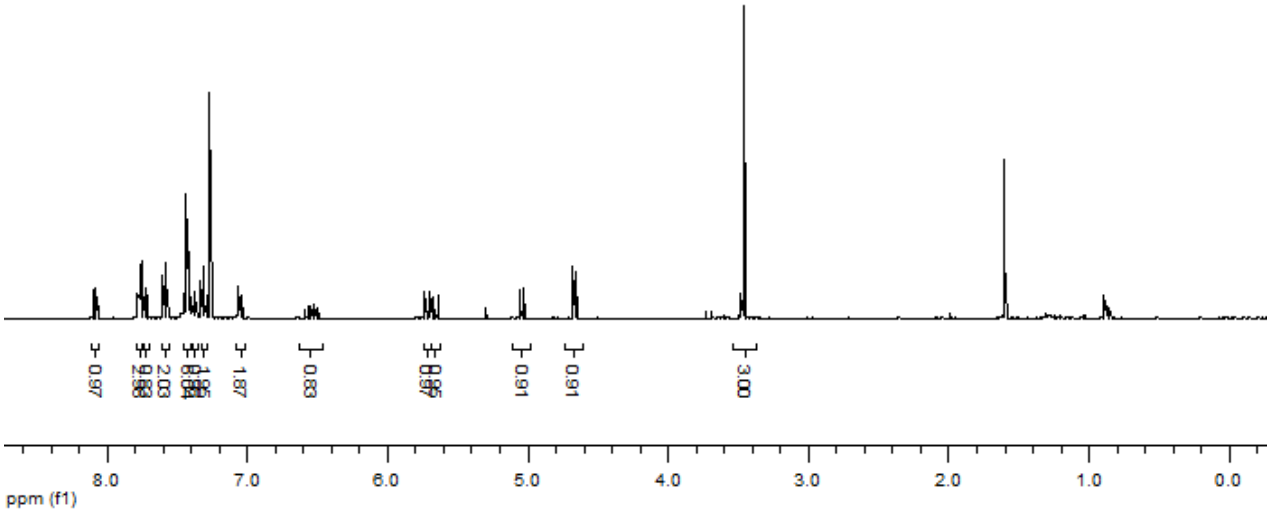

1.20
1.90
1.04
0.97
0.88
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

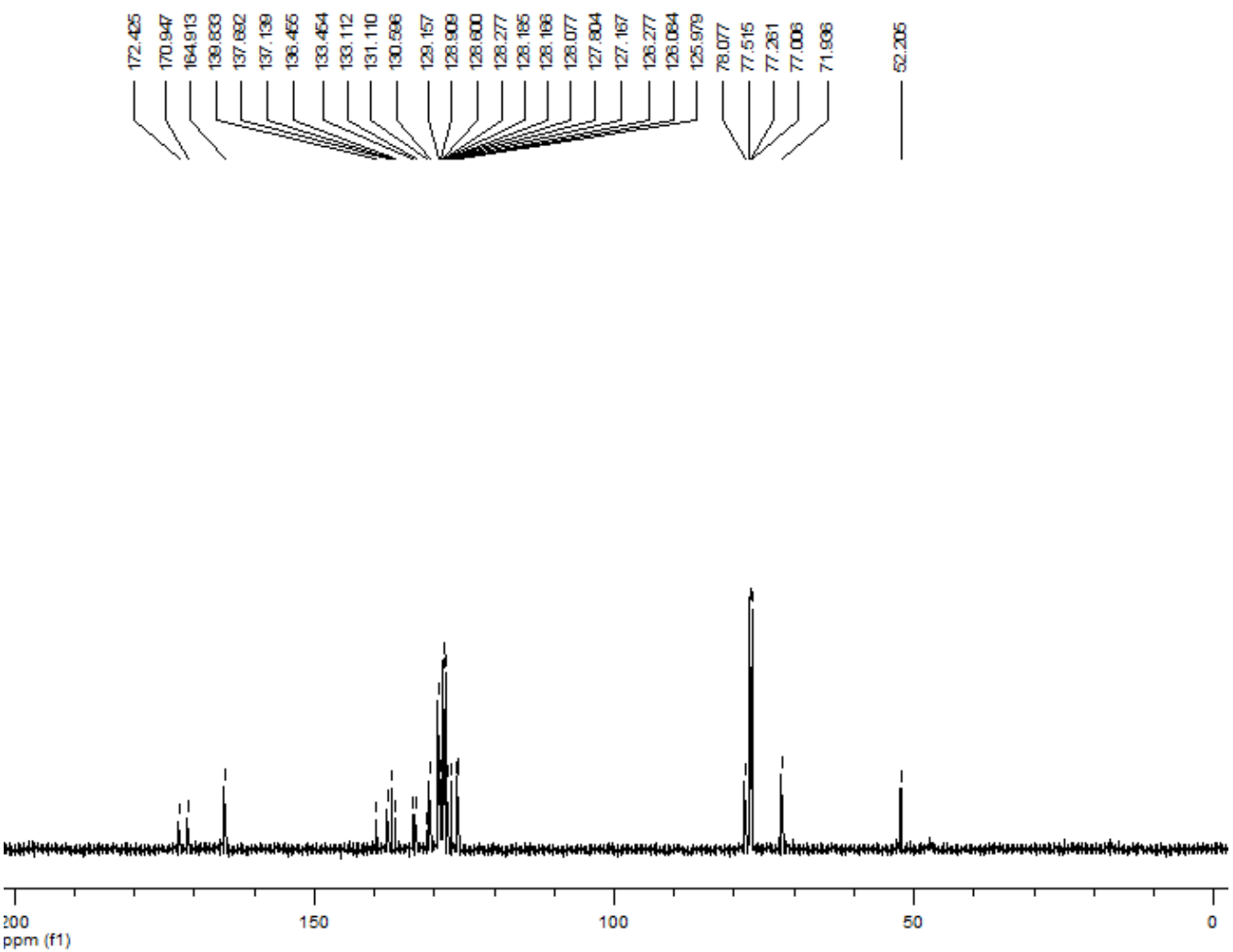

172.774
170.626
165.268
144.354
139.606
136.954
136.929
136.279
135.623
130.759
130.031
129.774
129.131
128.737
128.643
128.230
128.187
128.048
125.427
125.170
123.037
77.515
77.260
77.006
71.721
52.325

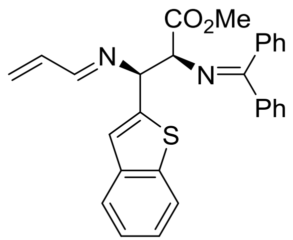

150
100
50
0
ppm (f1)


CO2Me
Ph
N
N
Ph

3m

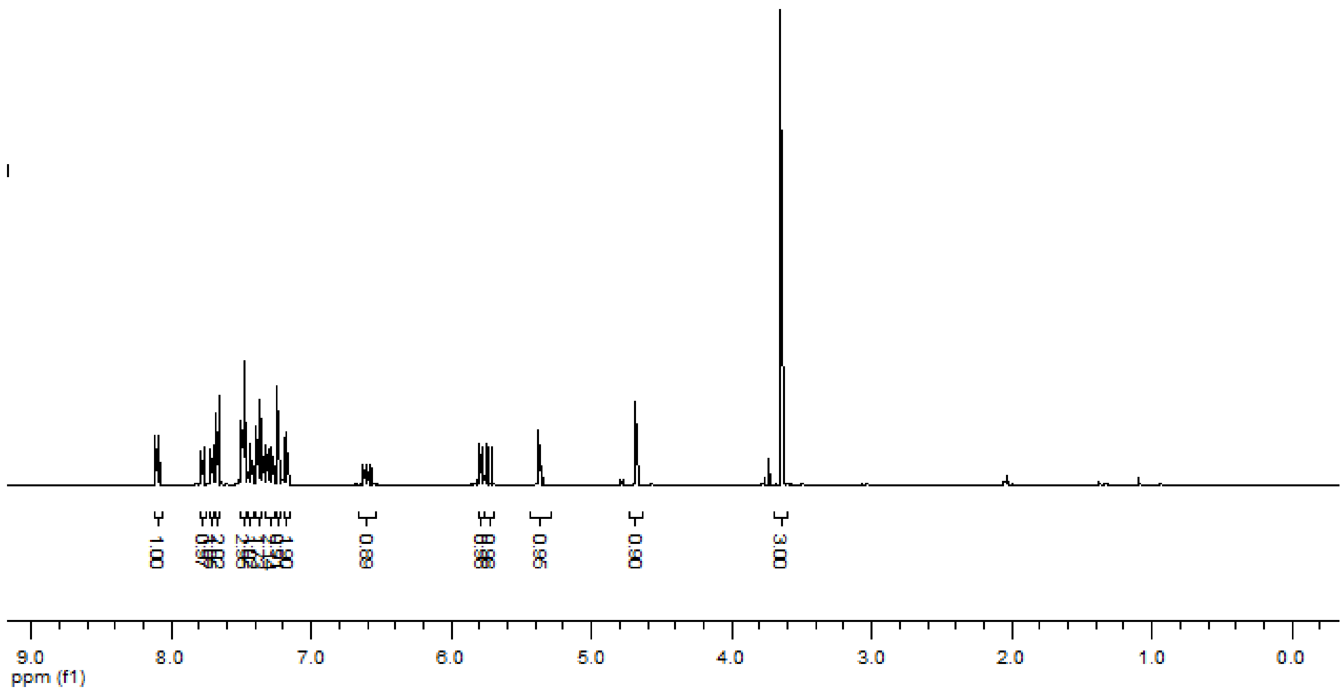

0.97
2.03
1.87
0.83
0.91
0.91
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


172.425
170.947
164.913
139.833
137.892
137.139
136.455
133.454
133.112
131.110
130.596
129.157
128.909
128.600
128.277
128.185
128.168
128.077
127.804
127.167
126.277
126.084
125.979
78.077
77.515
77.261
77.006
71.936
52.205
200
150
100
50
0
ppm (f1)

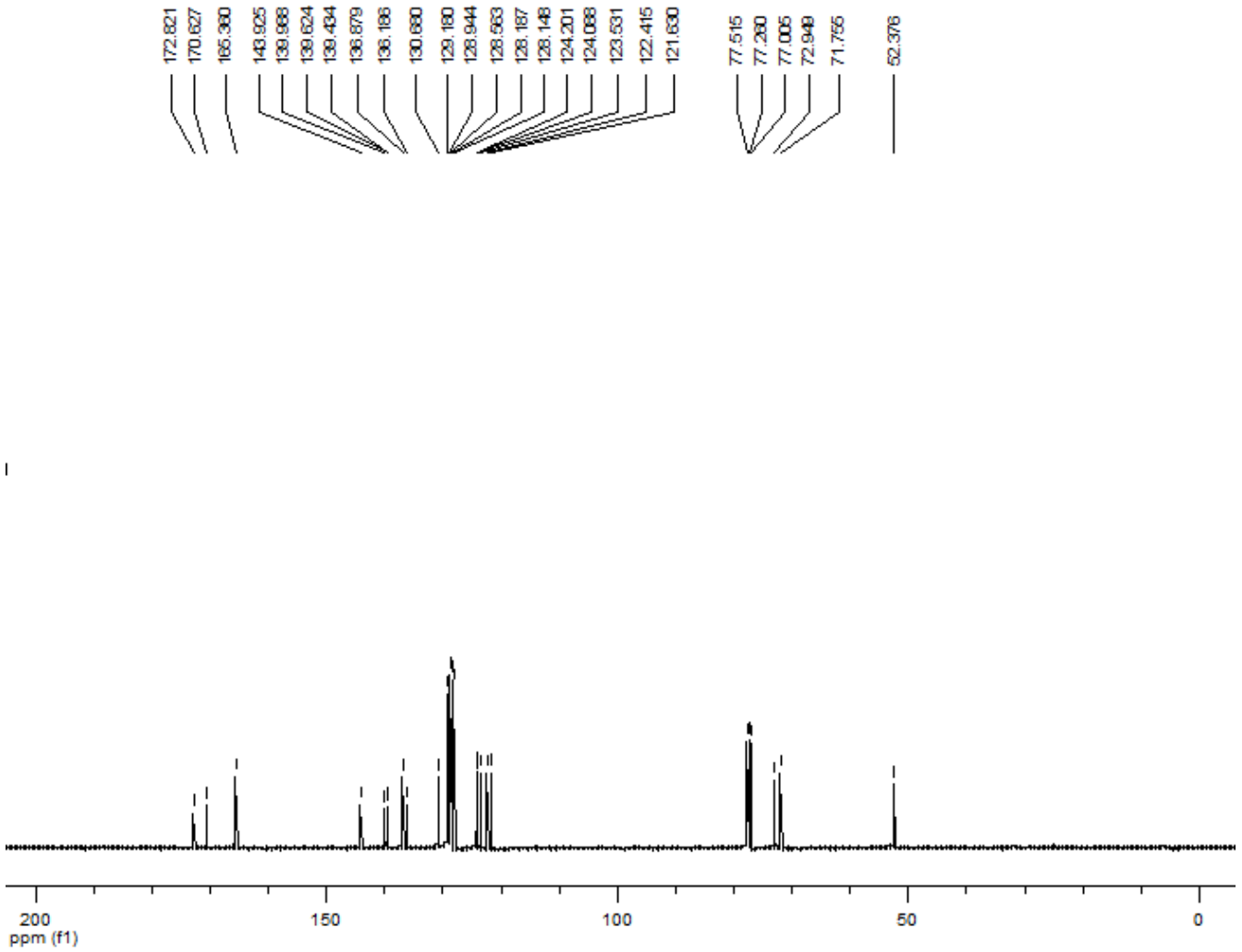


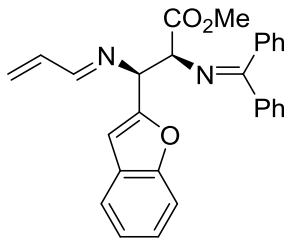
CO2Me
N
N
Ph
Ph
S

3n

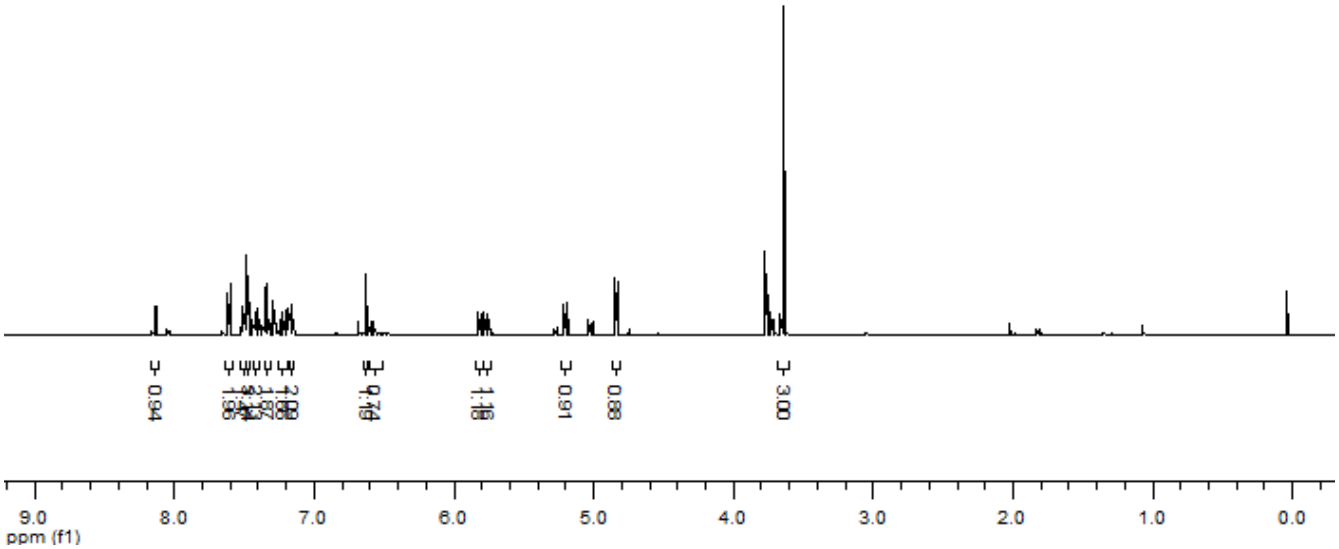


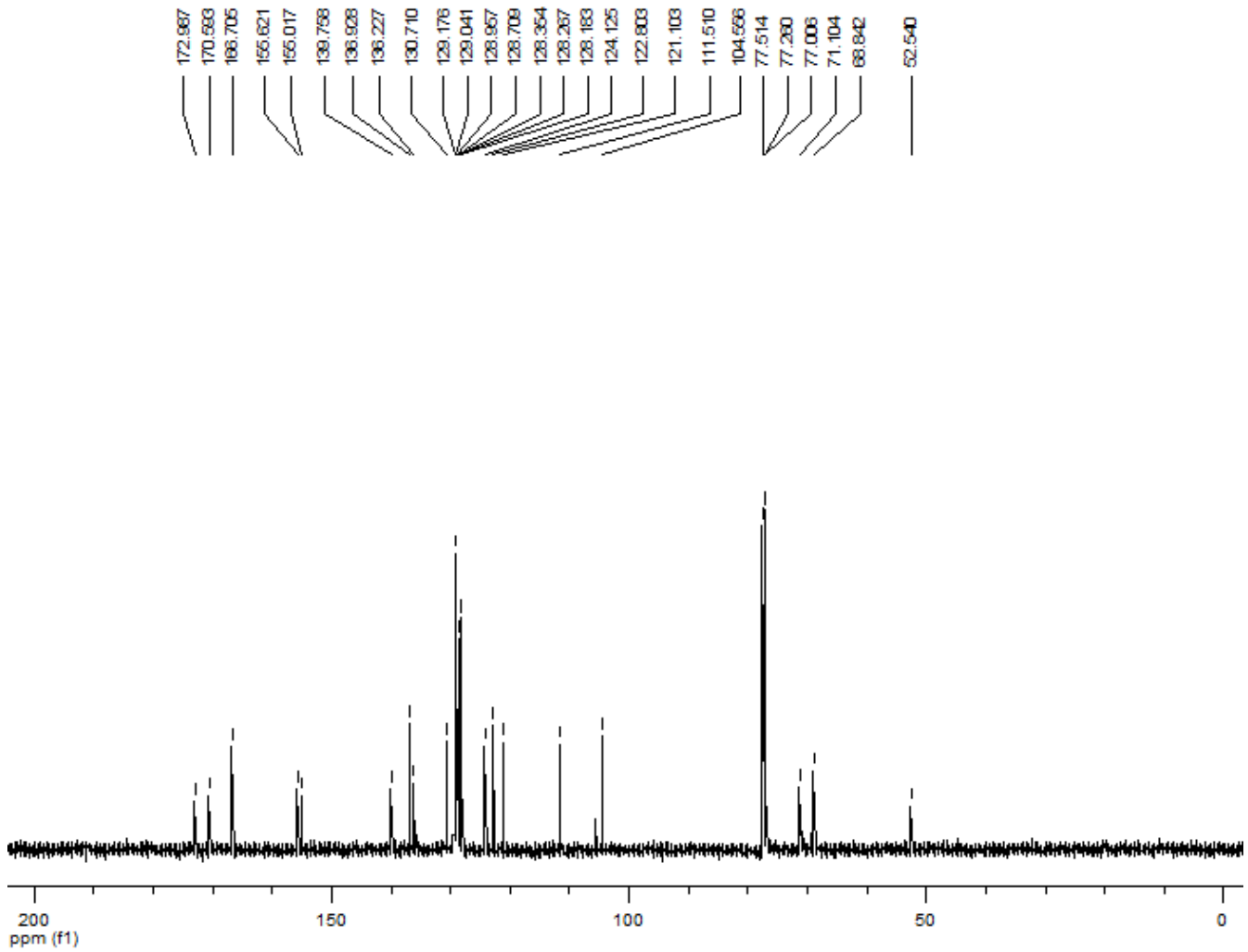
1.00
0.97
0.95
2.02
2.06
1.05
1.02
1.03
0.98
0.84
1.00
0.89
0.86
0.86
0.95
0.90
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

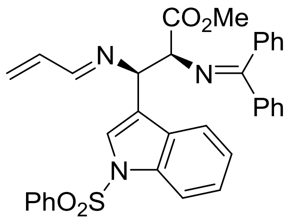

172.821
170.627
165.390
143.925
139.988
139.624
139.434
136.879
136.186
130.680
129.180
128.944
128.563
128.187
128.148
124.201
124.088
123.531
122.415
121.630
77.515
77.260
77.005
72.949
71.755
52.376
200
ppm (f1)
150
100
50
0


CO2Me
Ph
N
N
Ph
O

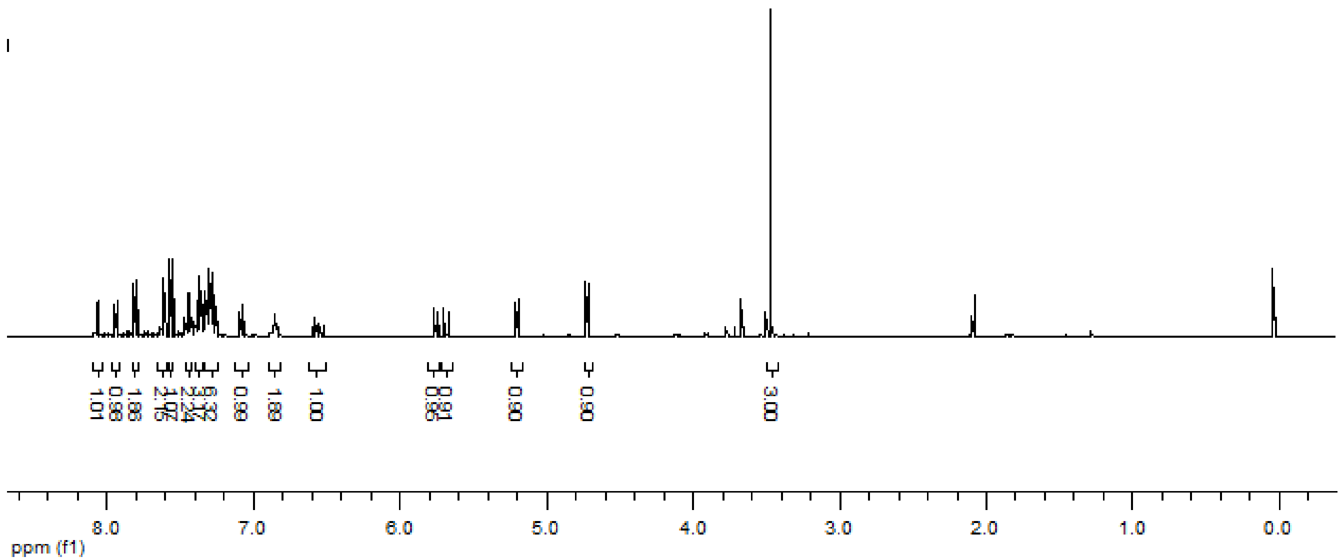
3o

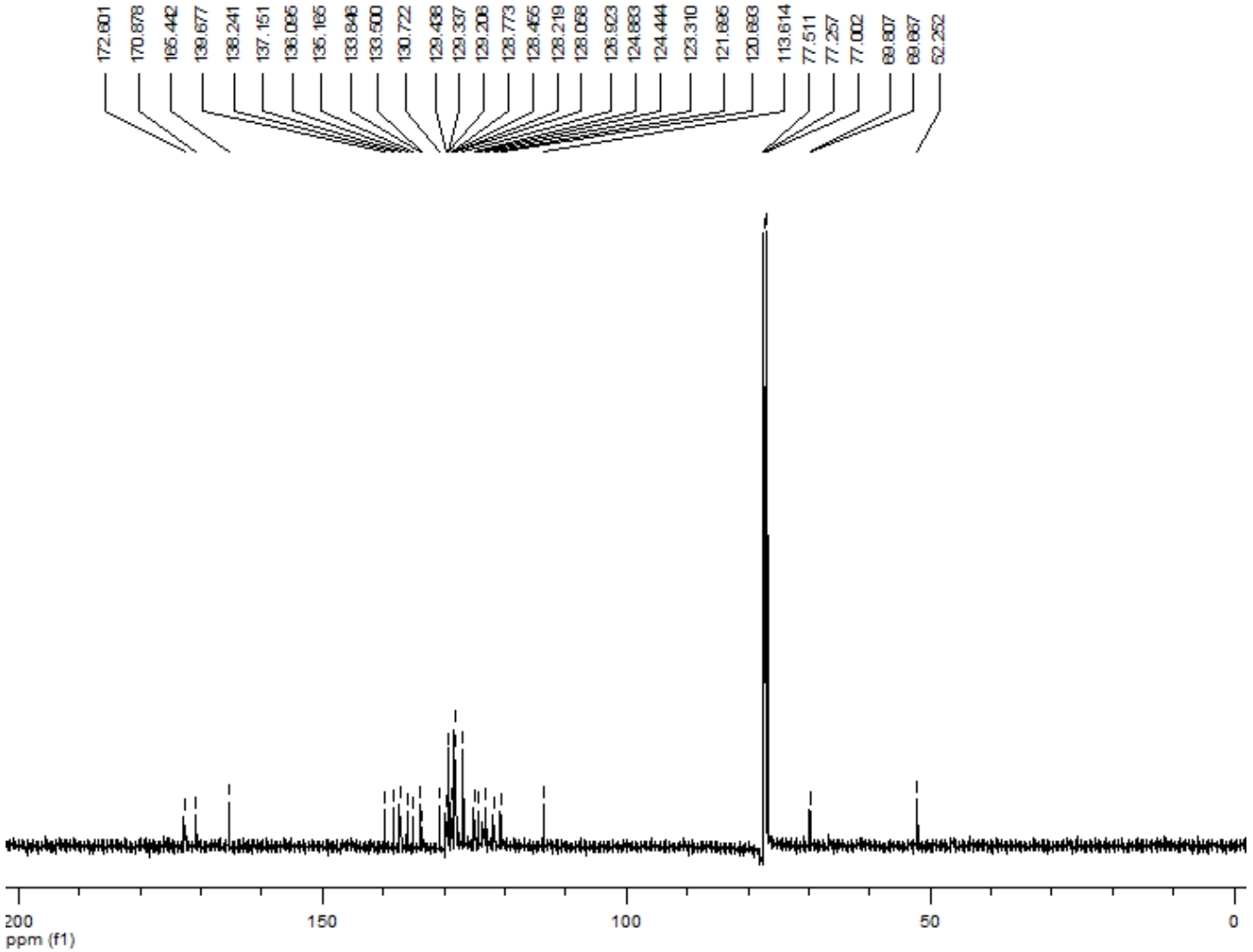

0.94
2.00
0.74
1.16
0.91
0.88
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

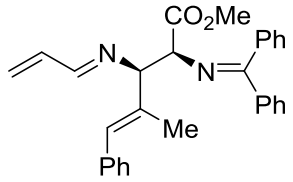

172.987
170.593
166.705
155.621
155.017
139.758
136.928
136.227
130.710
129.176
129.041
128.957
128.709
128.354
128.267
128.183
124.125
122.803
121.103
111.510
104.556
77.514
77.260
77.006
71.104
68.842
52.540
200
150
100
50
0
ppm (f1)



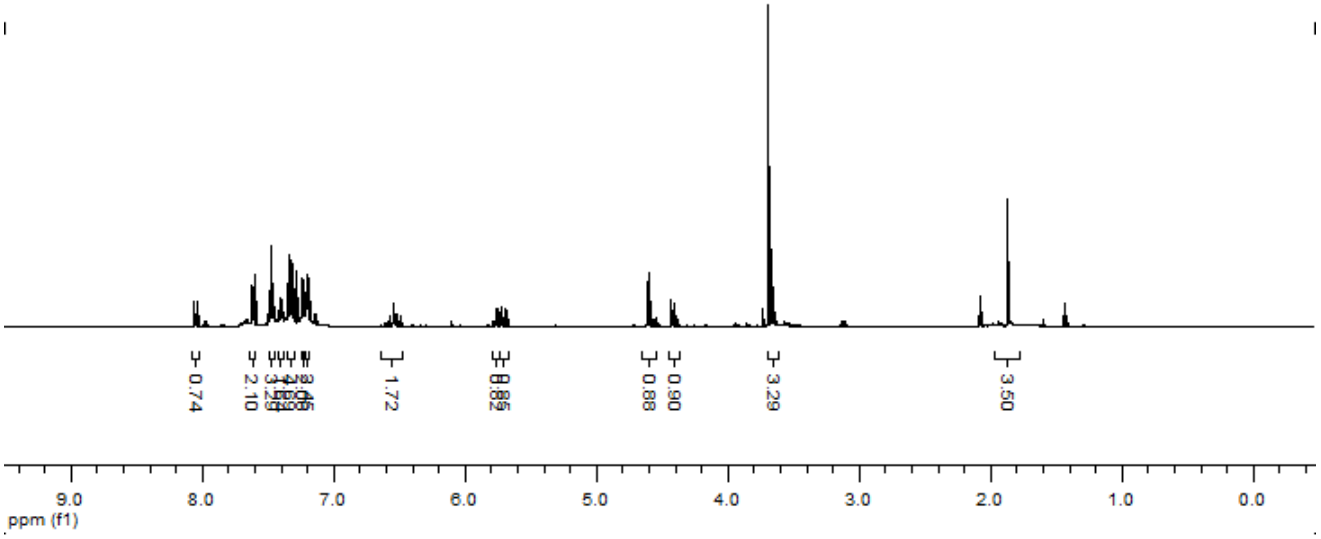
3p

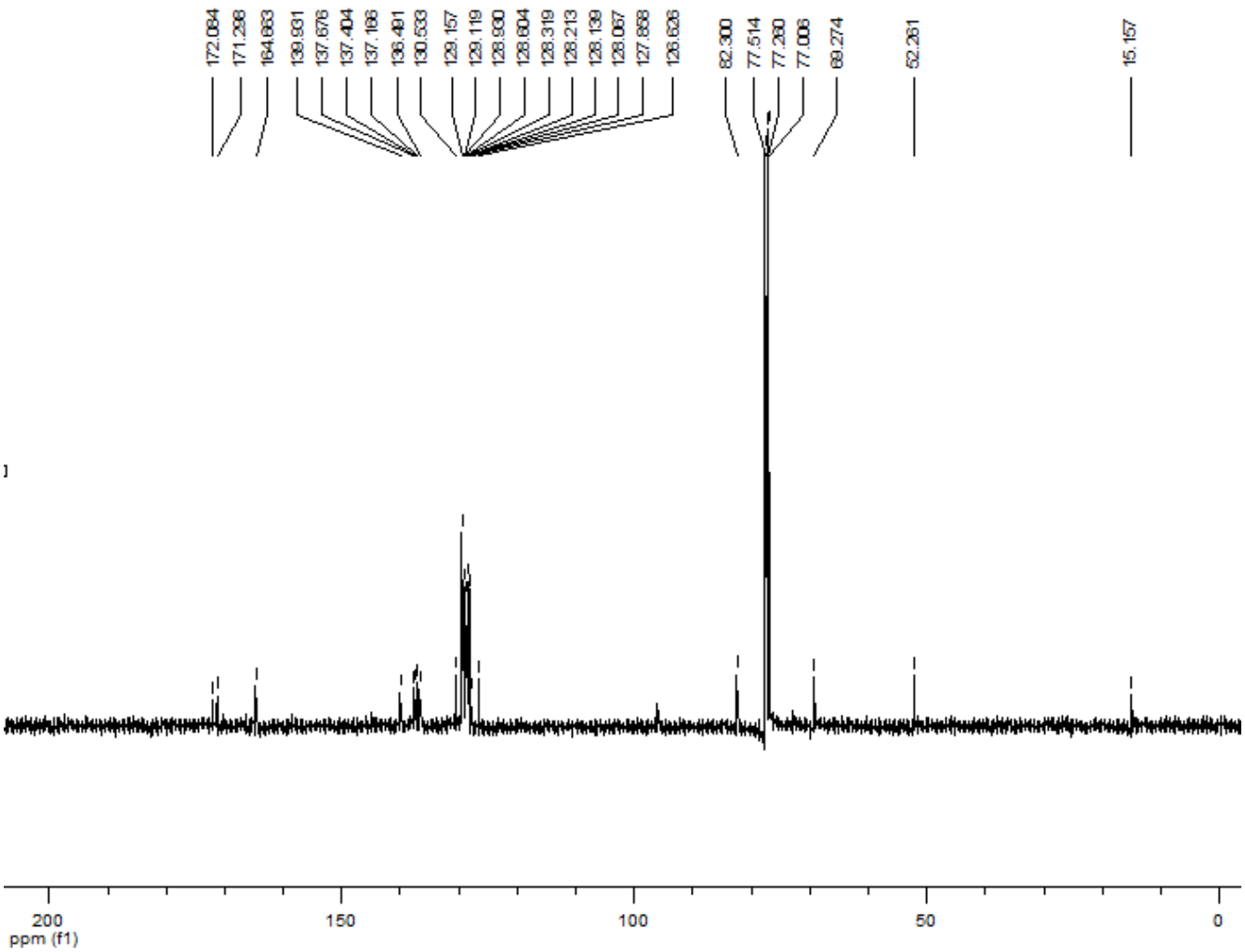


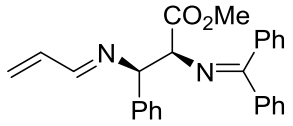

172.601
170.878
166.442
139.677
138.241
137.151
136.095
135.165
133.846
133.600
130.722
129.438
129.337
129.206
128.773
128.455
128.219
128.058
126.923
124.883
124.444
123.310
121.885
120.883
113.614
77.511
77.257
77.002
69.807
69.667
52.252
200
ppm (f1)
150
100
50
0


CO2Me
N
N
Ph
Ph
Me
Ph

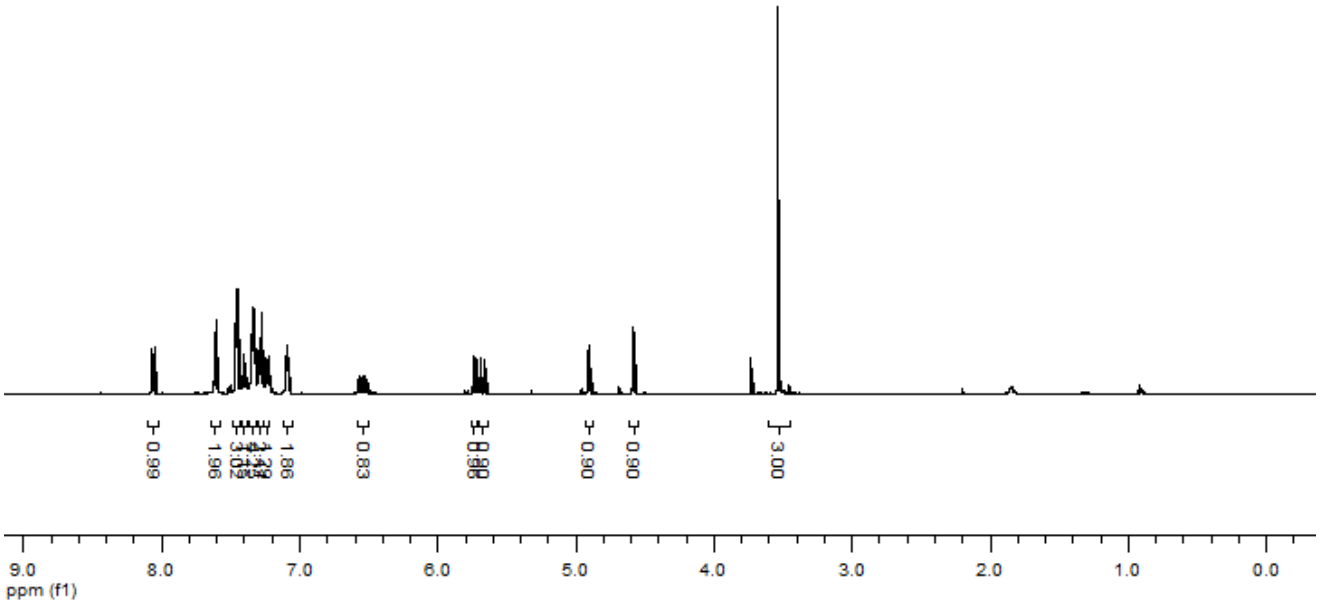
3q

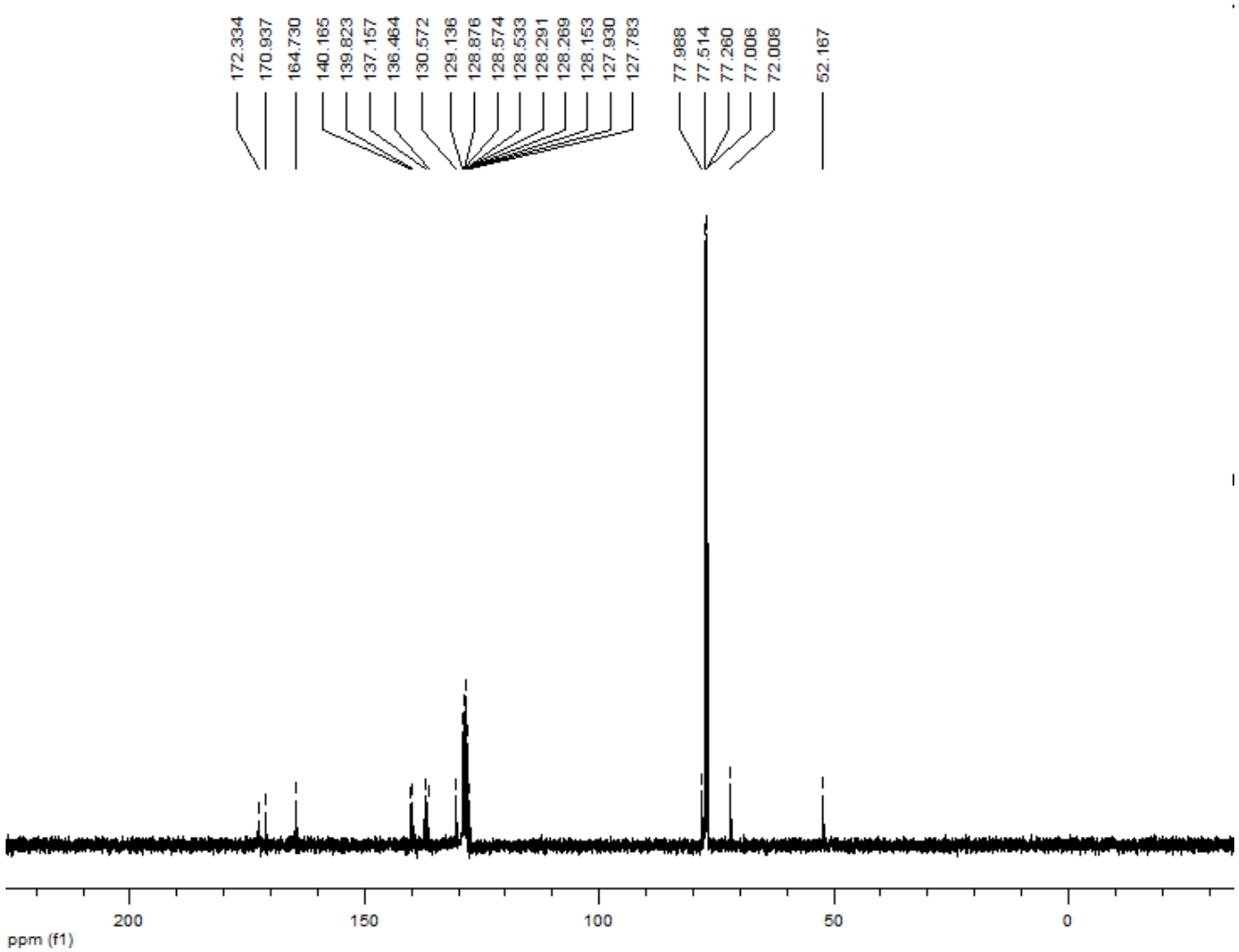

0.74
2.10
1.72
0.88
0.90
3.29
3.50
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

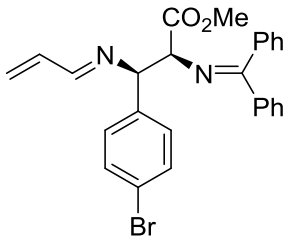

172.084
171.298
164.863
139.931
137.676
137.404
137.186
136.491
130.533
129.157
129.119
128.930
128.604
128.319
128.213
128.139
128.067
127.868
126.626
82.300
77.514
77.200
77.006
69.274
52.261
15.157
200
150
100
50
0
ppm (f1)


CO2Me
Ph
N
N
Ph
Ph

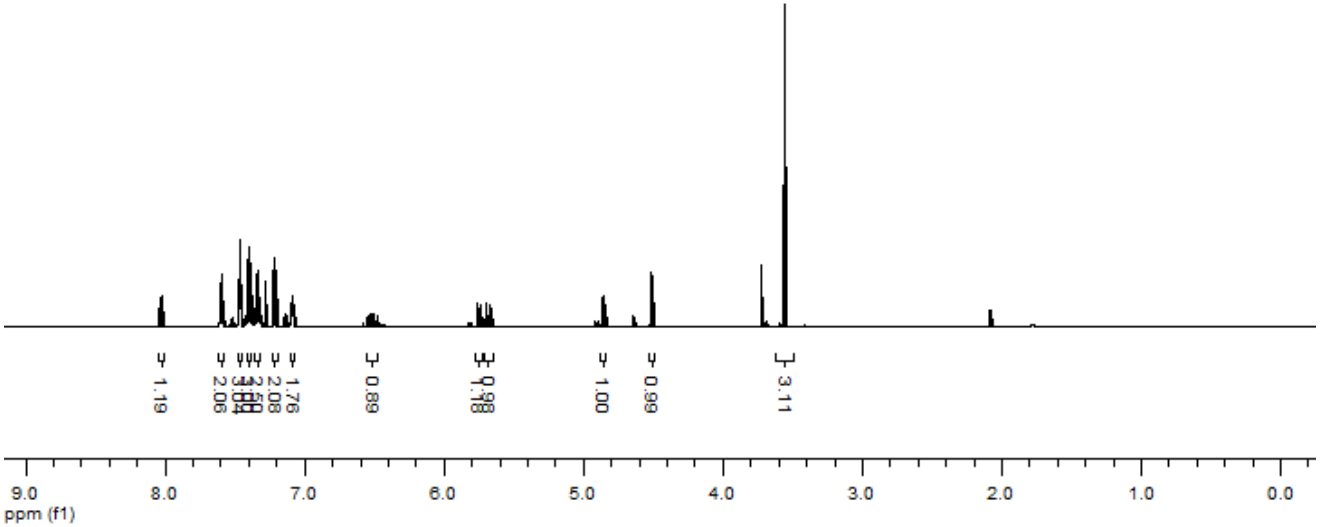
6a

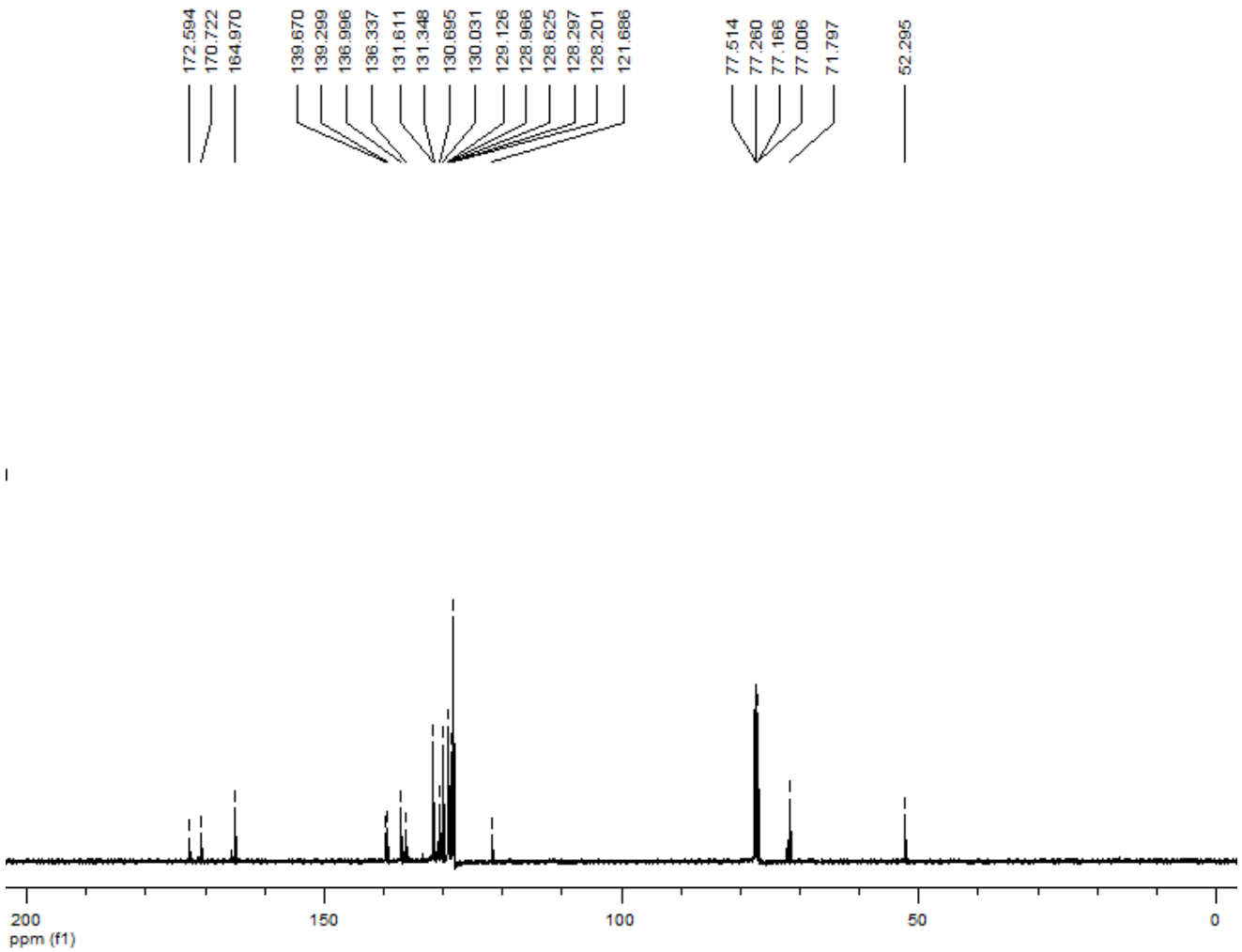

0.99
1.96
1.86
0.83
0.90
0.90
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

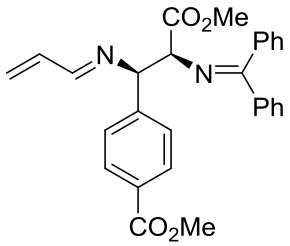

172.334
170.937
164.730
140.165
139.823
137.157
136.464
130.572
129.136
128.876
128.574
128.533
128.291
128.269
128.153
127.930
127.783
77.988
77.514
77.260
77.006
72.008
52.167
200
150
100
50
0
ppm (f1)


CO2Me
Ph
N
N
Ph
Br

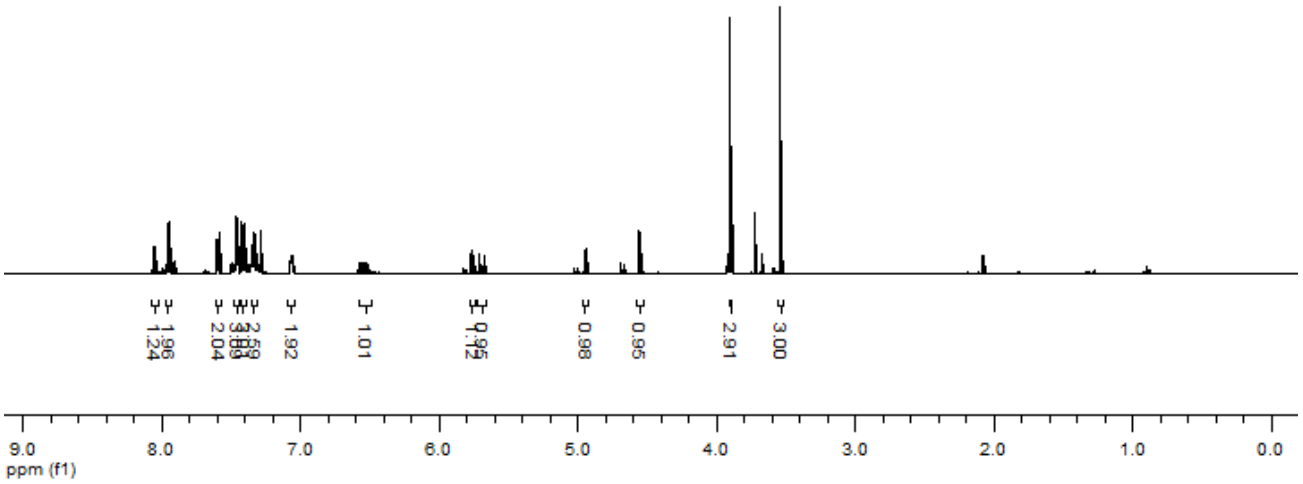
6b

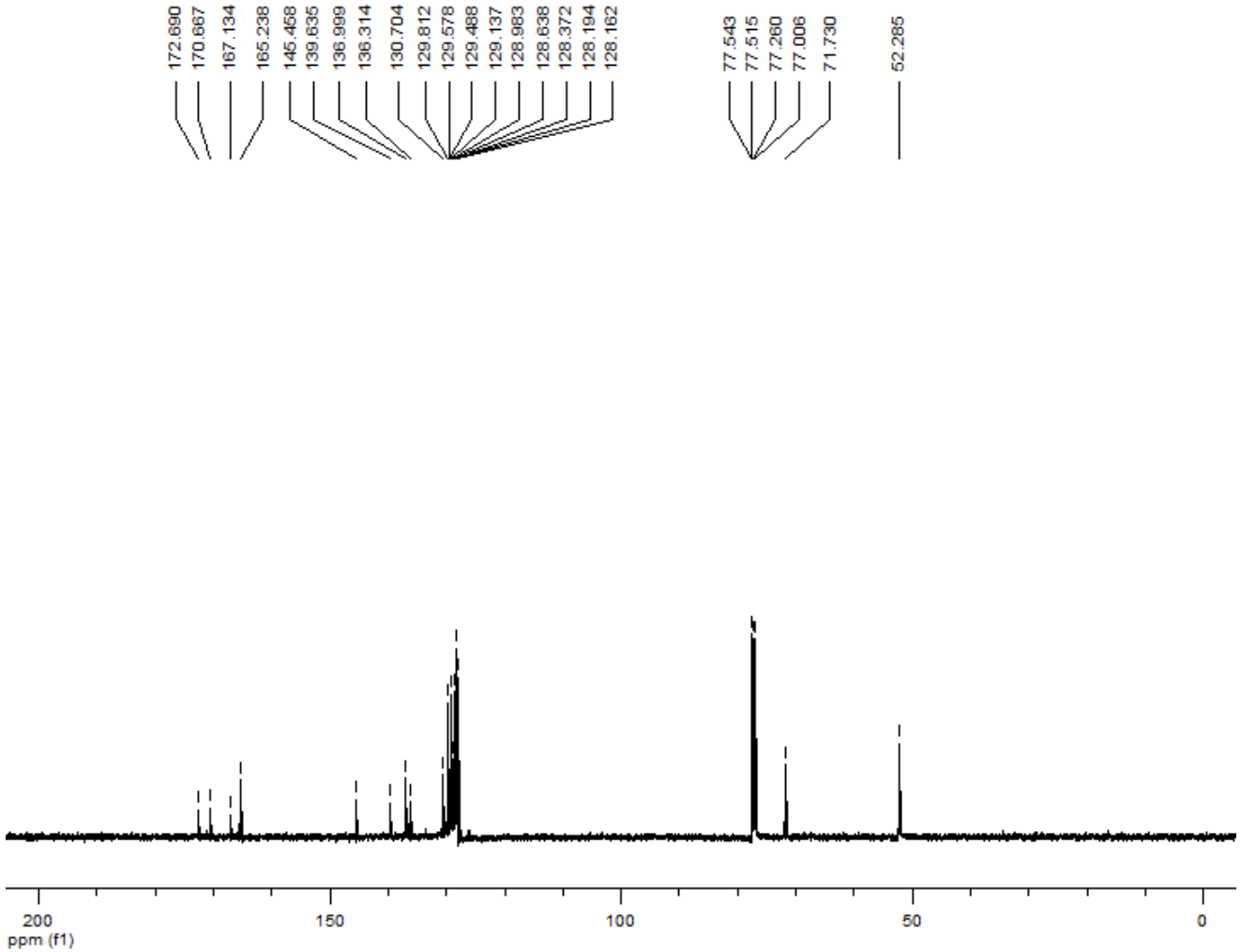

1.19
2.06
2.08
1.76
0.89
0.98
1.00
0.99
3.11
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

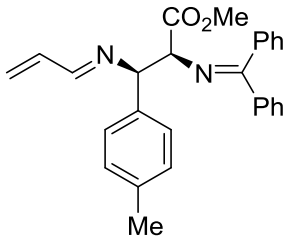

172.594
170.722
164.970
139.670
139.299
136.996
136.337
131.611
131.348
130.695
130.031
129.126
128.966
128.625
128.297
128.201
121.686
77.514
77.260
77.166
77.006
71.797
52.295
200
150
100
50
0
ppm (f1)


CO2Me
Ph
N
N
Ph
CO2Me

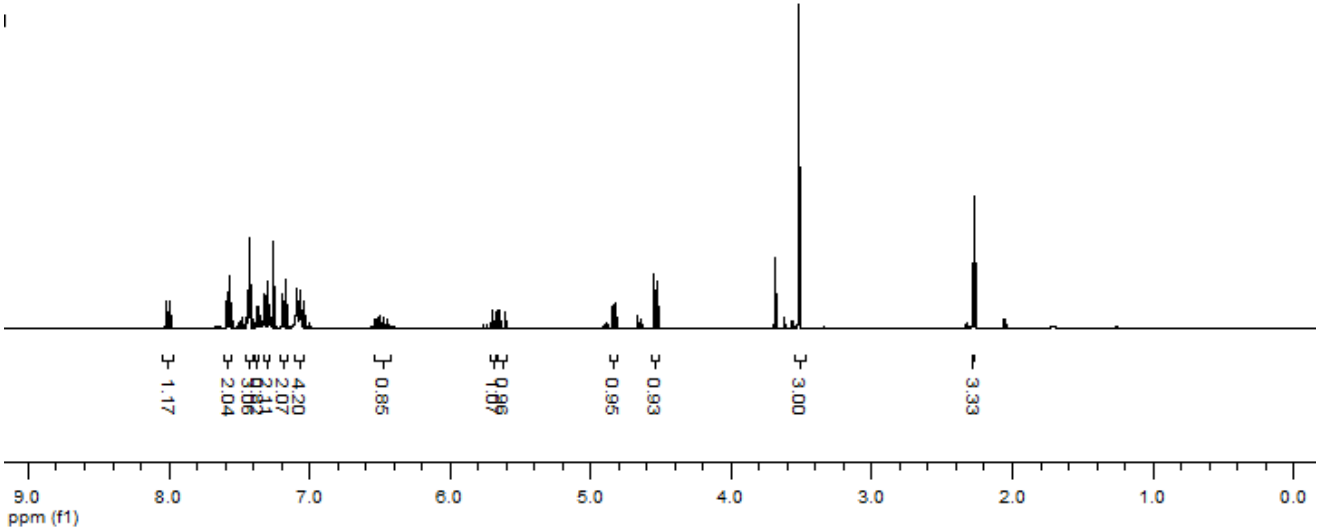
6c

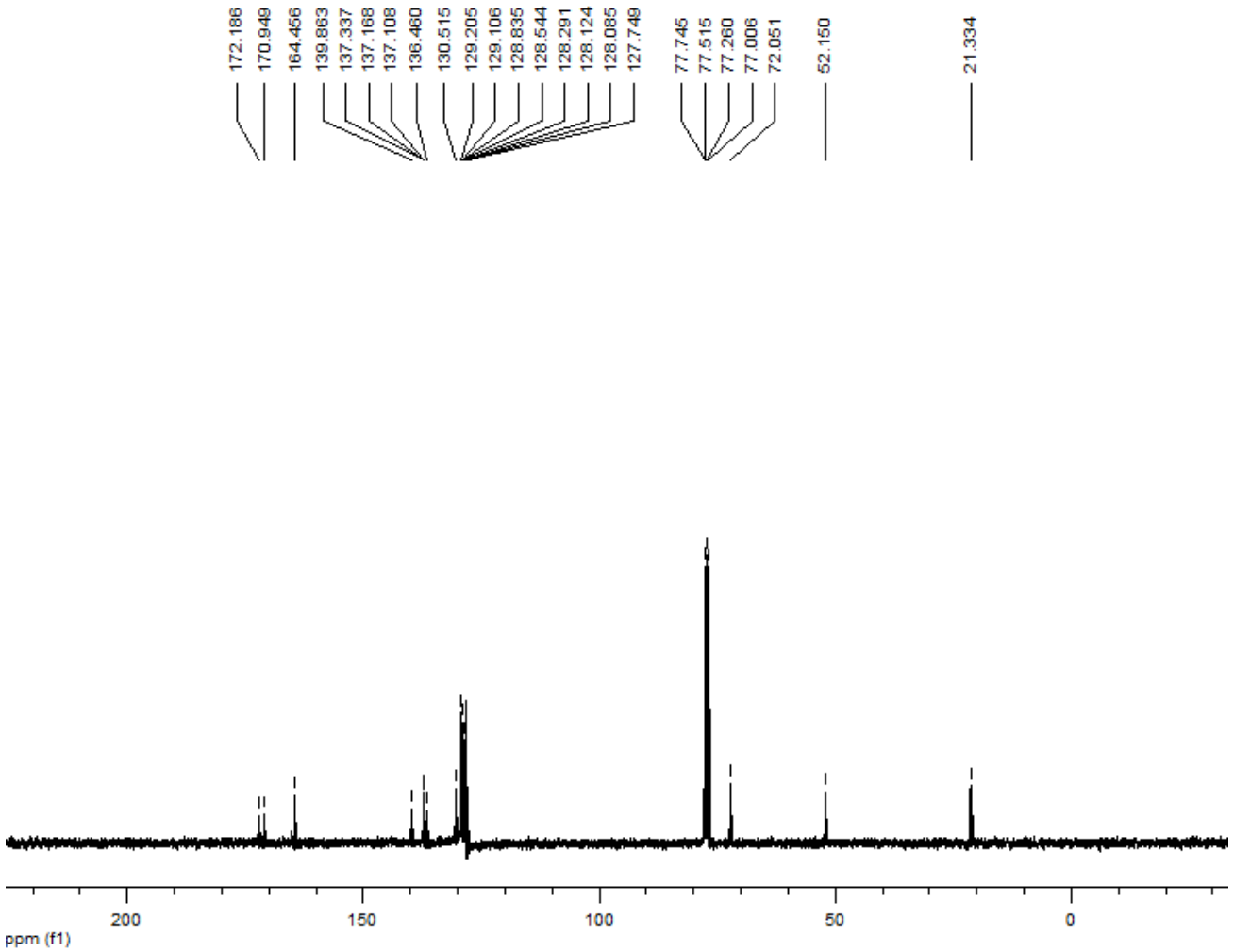

1.24
1.96
2.04
1.92
1.01
0.95
0.98
0.95
2.91
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

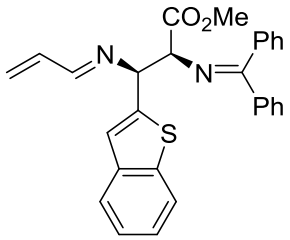

172.690
170.667
167.134
165.238
145.458
139.635
136.999
136.314
130.704
129.812
129.578
129.488
129.137
128.983
128.638
128.372
128.194
128.162
77.543
77.515
77.260
77.006
71.730
52.285
200
150
100
50
0
ppm (f1)


CO2Me
Ph
N
N
Ph
Me

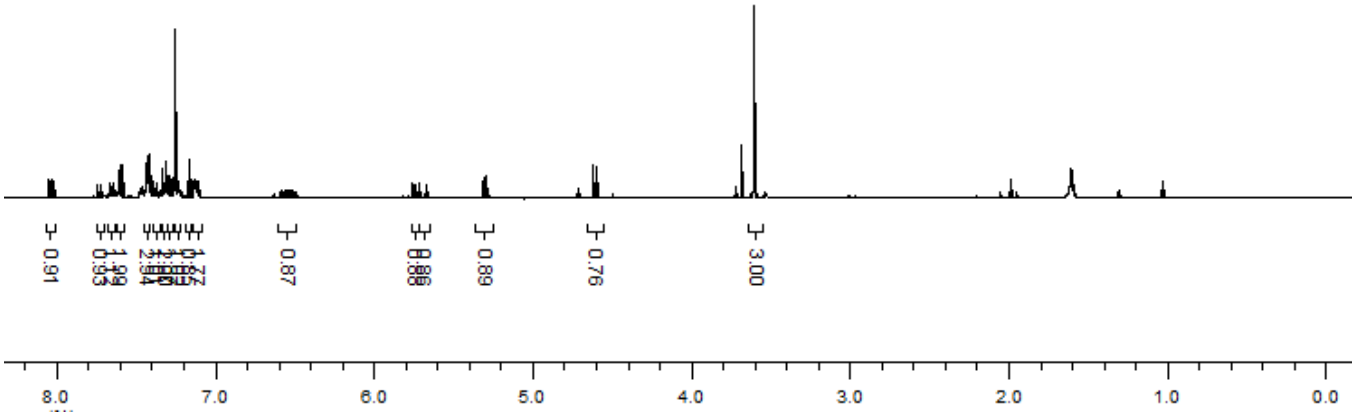
6d

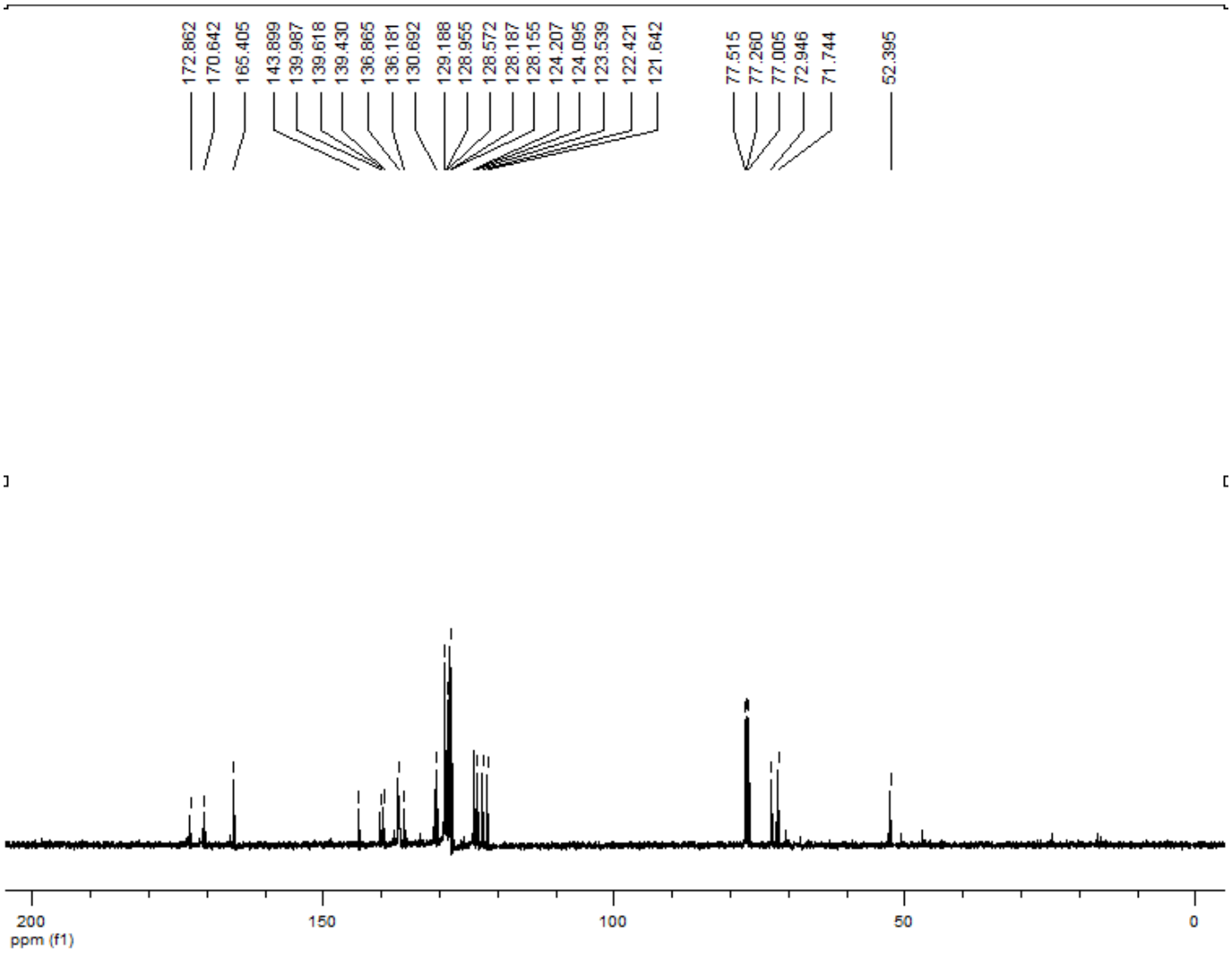

1.17
2.04
4.20
2.07
0.85
0.95
0.93
3.00
3.33
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

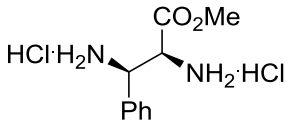

172.186
170.949
164.456
139.863
137.337
137.168
137.108
136.460
130.515
129.205
129.106
128.835
128.544
128.291
128.124
128.085
127.749
77.745
77.515
77.260
77.006
72.051
52.150
21.334
200
150
100
50
0
ppm (f1)


CO2Me
Ph
N
N
Ph
S

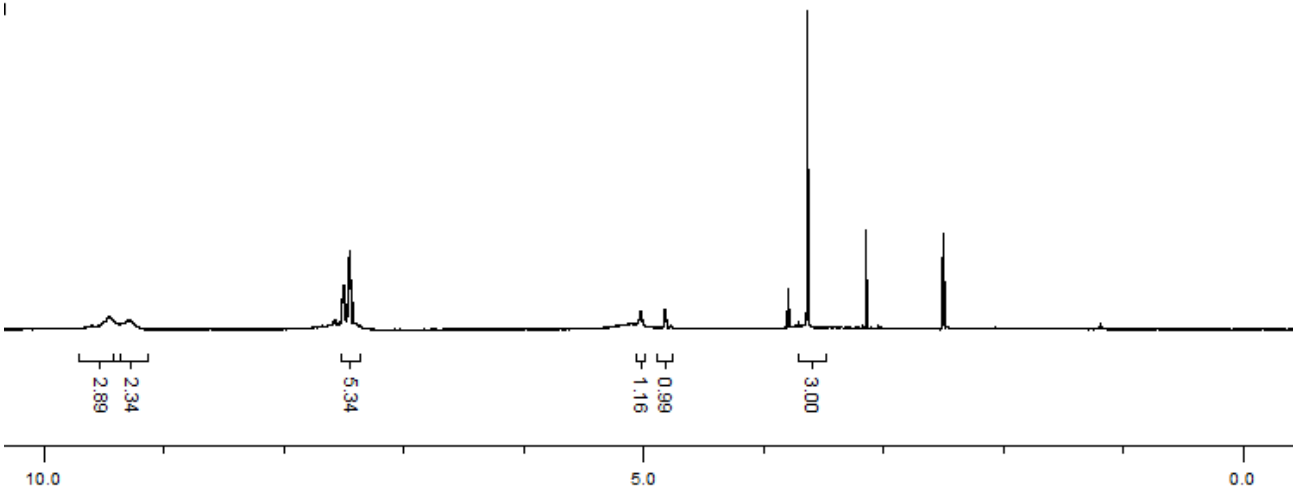
6e

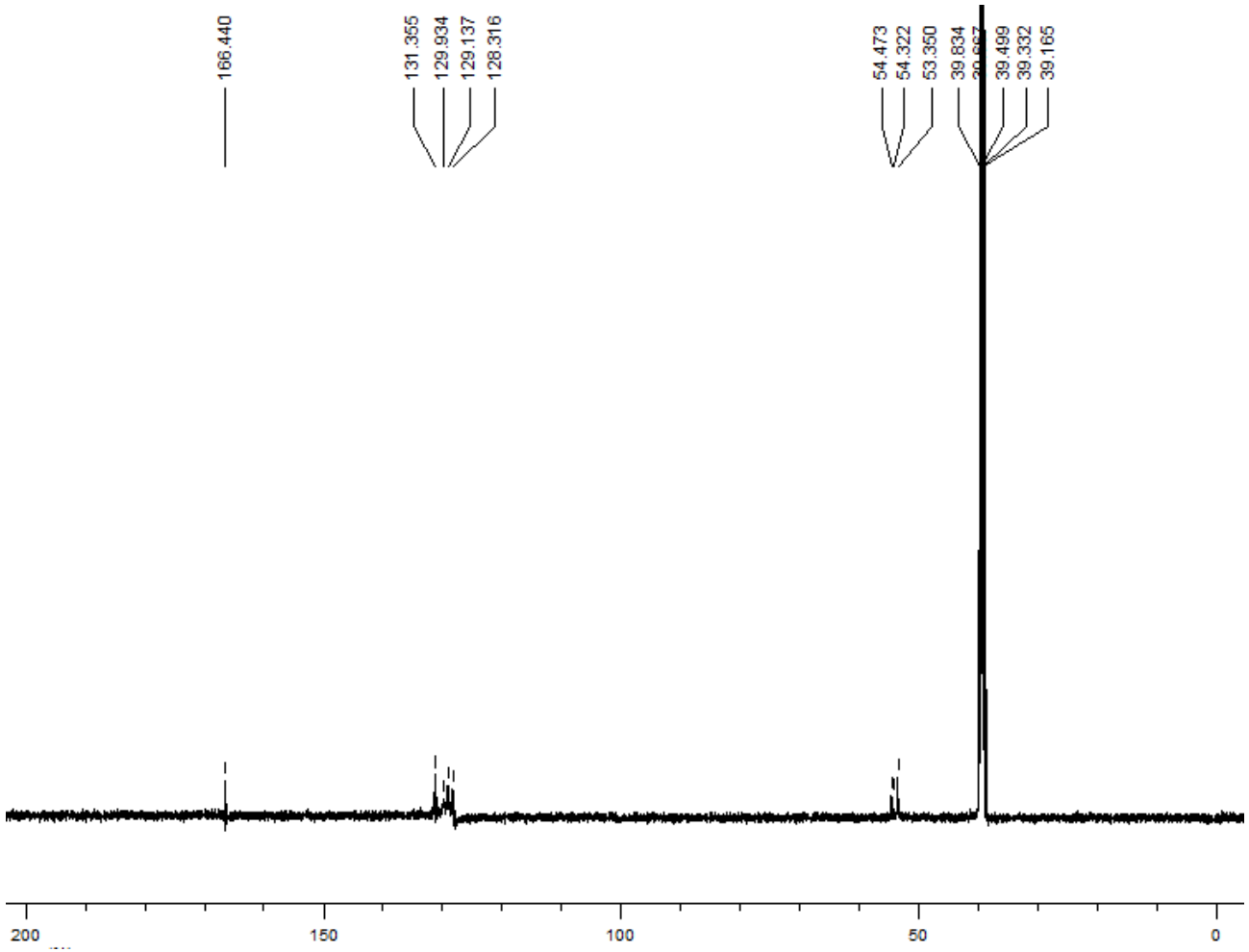

0.91
1.99
0.93
0.87
0.89
0.76
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

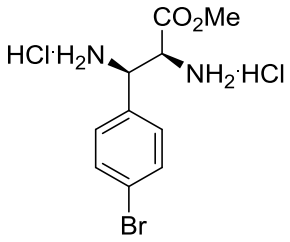

172.862
170.642
165.405
143.899
139.987
139.618
139.430
136.865
136.181
130.692
129.188
128.955
128.572
128.187
128.155
124.207
124.095
123.539
122.421
121.642
77.515
77.260
77.005
72.946
71.744
52.395
200
ppm (f1)
150
100
50
0



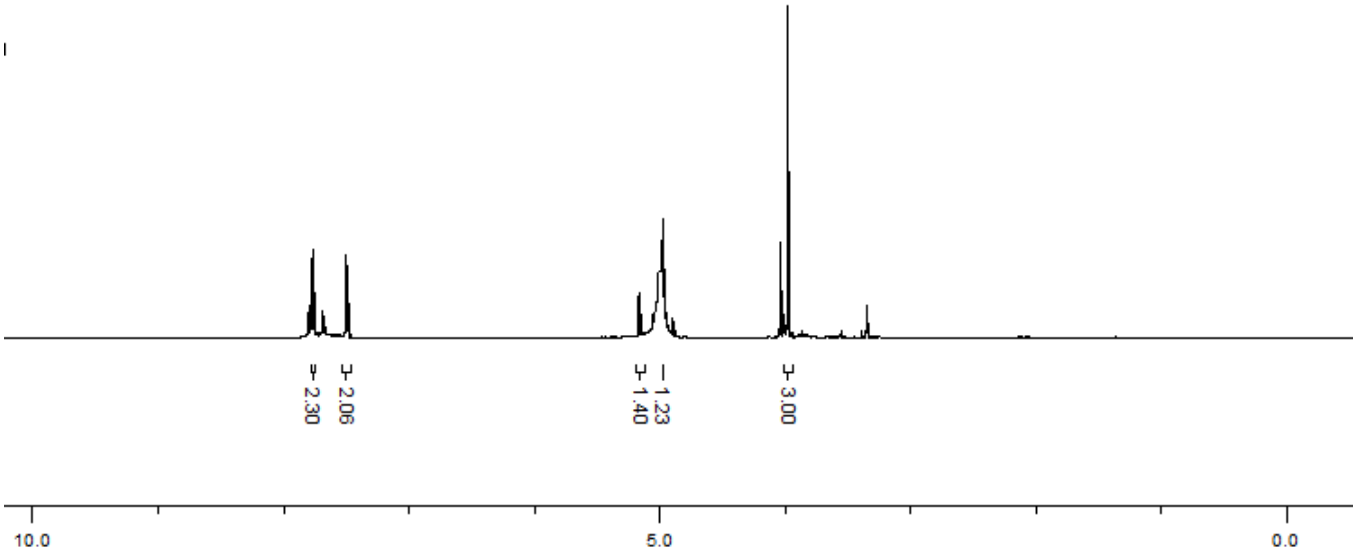
7a

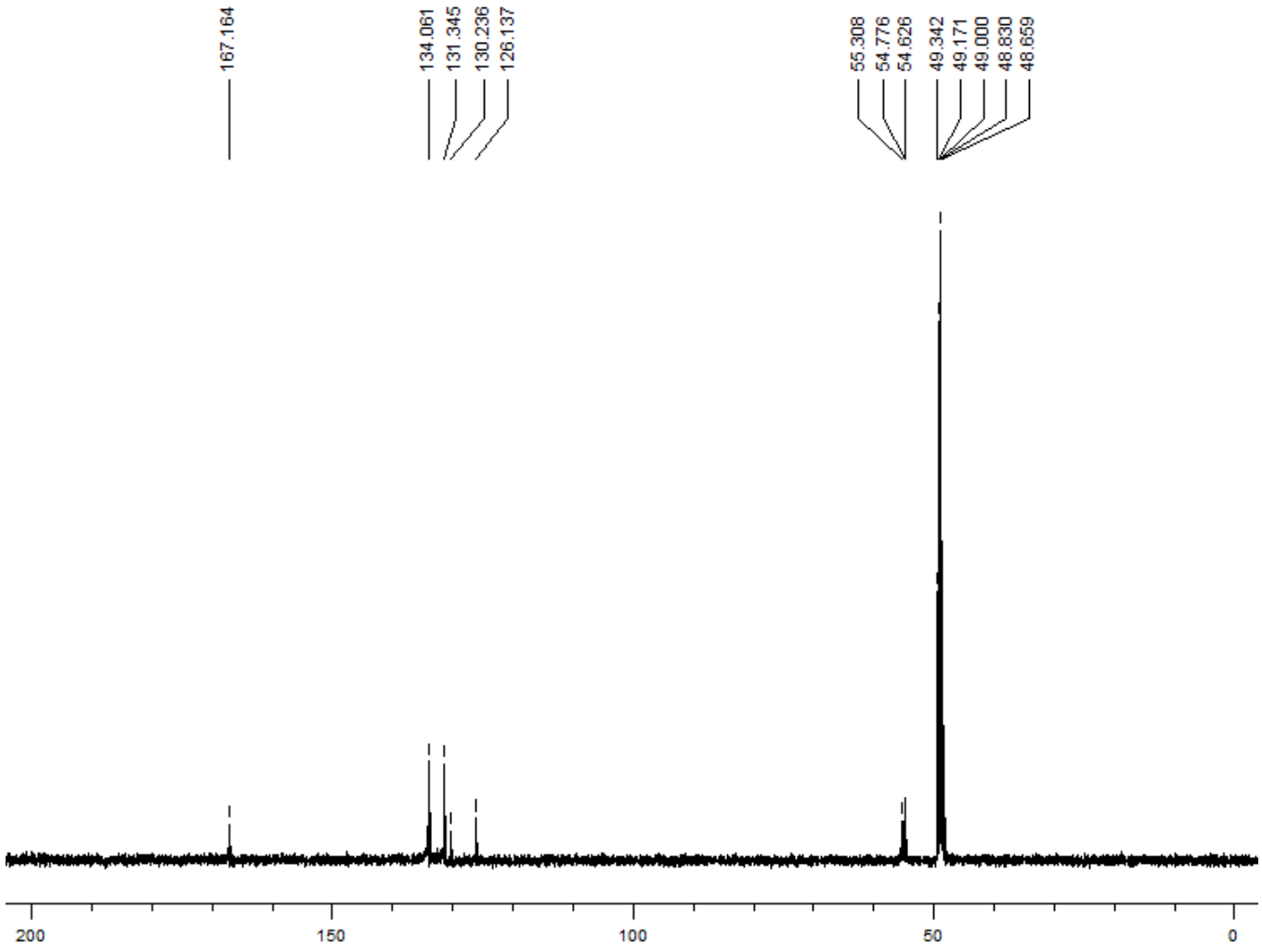


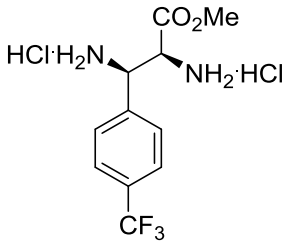

166.440
131.355
129.934
129.137
128.316
54.473
54.322
53.350
39.834
39.499
39.332
39.165
200
150
100
50
0



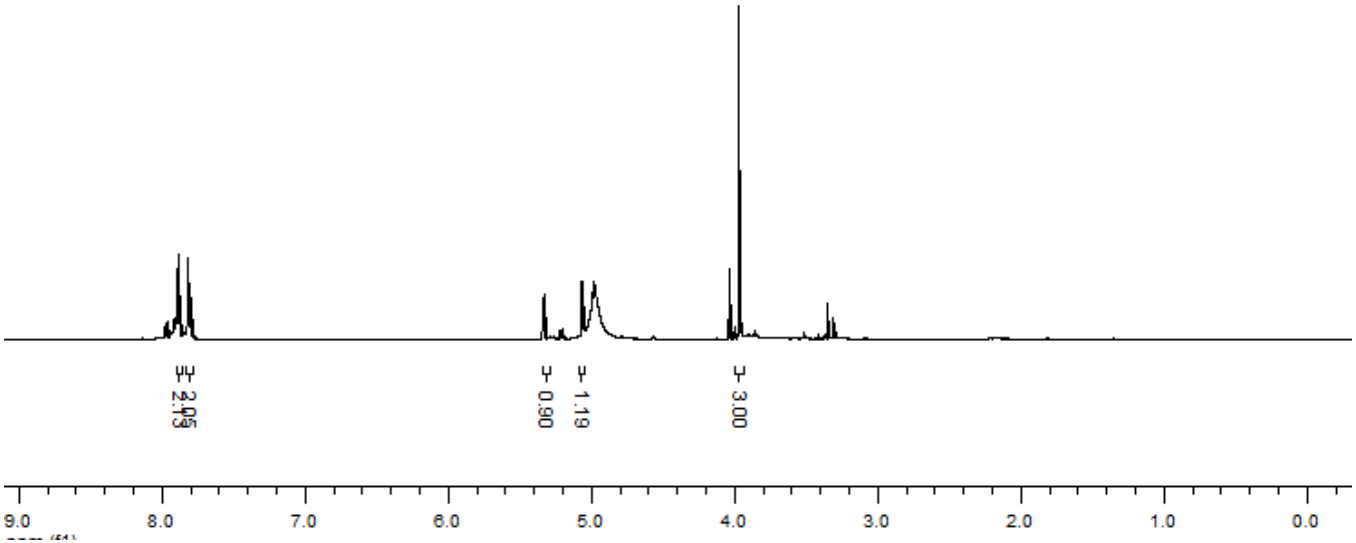
7b

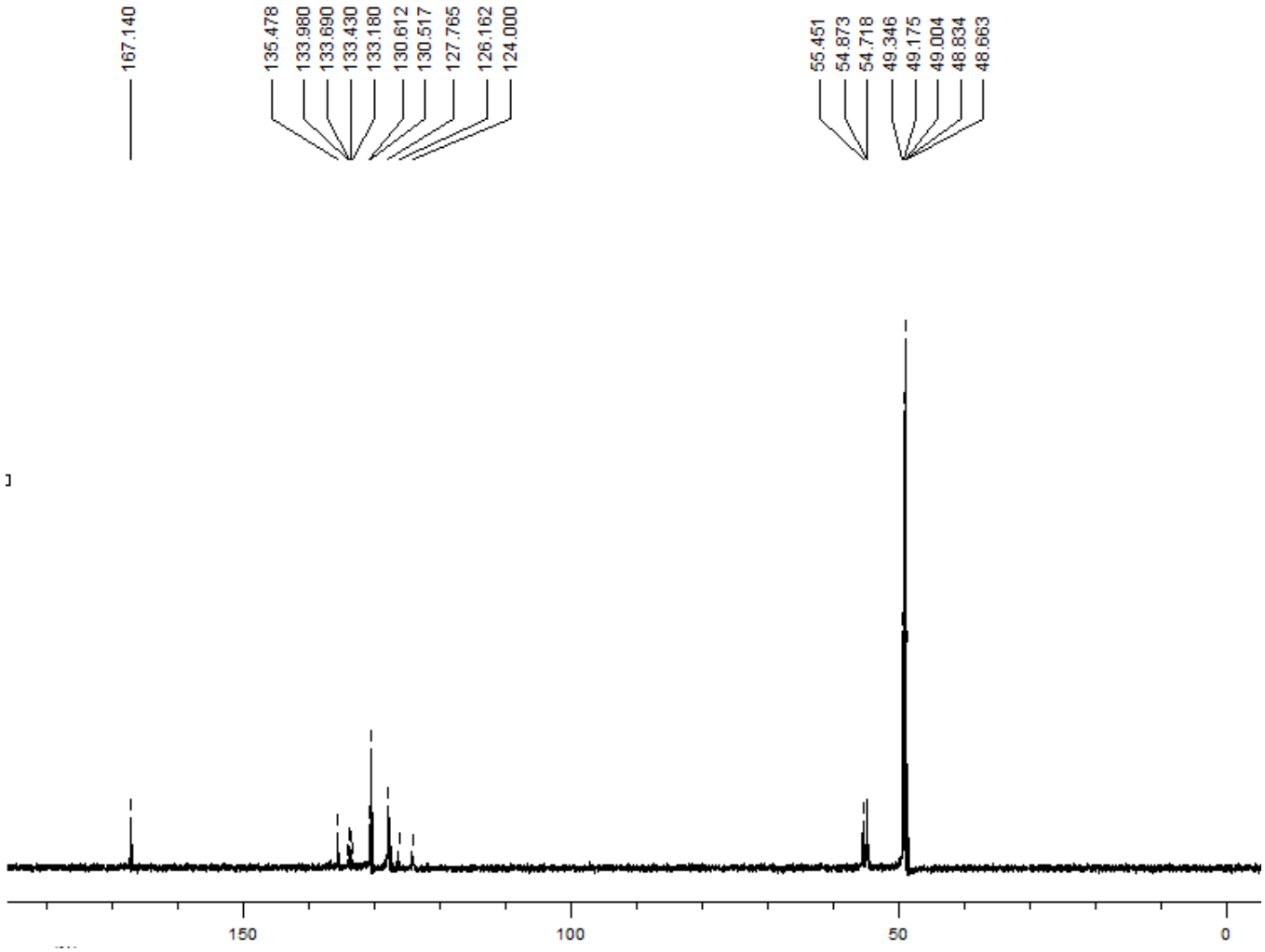


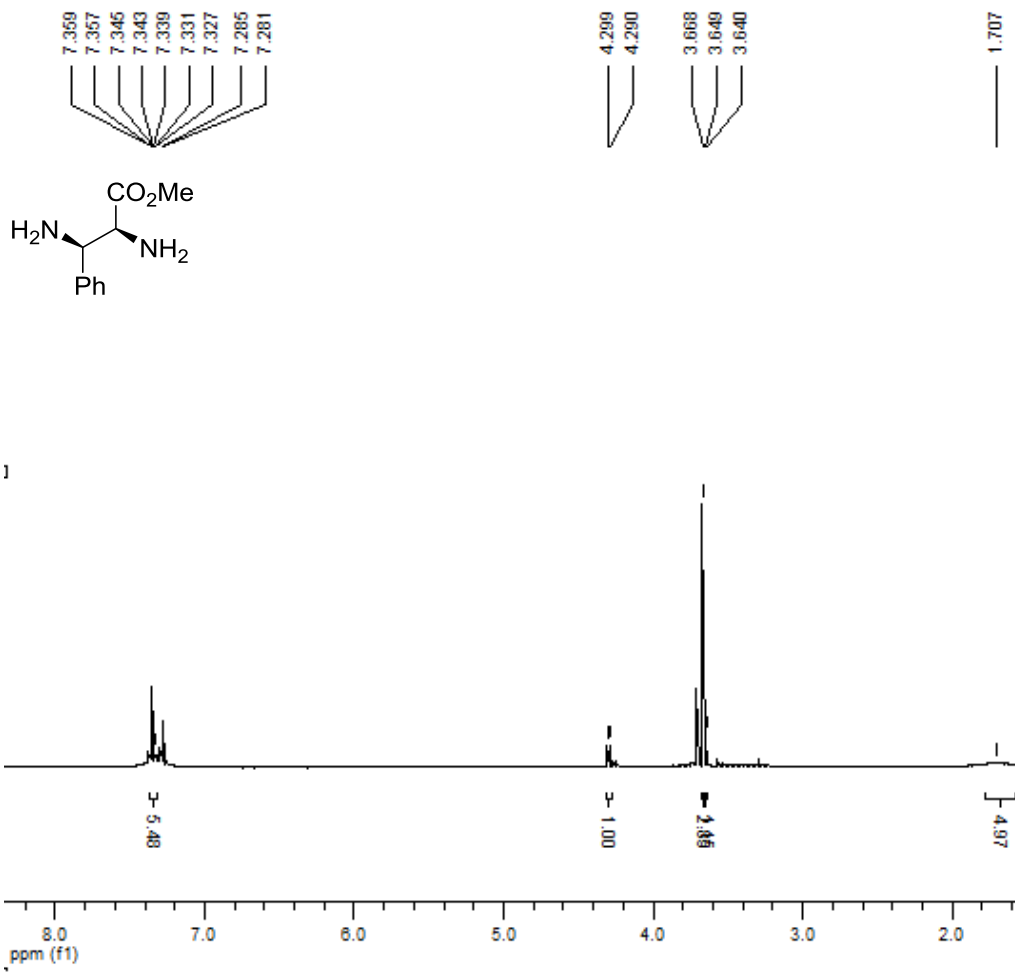

167.164
134.061
131.345
130.236
126.137
55.308
54.776
54.626
49.342
49.171
49.000
48.830
48.659
200
150
100
50
0

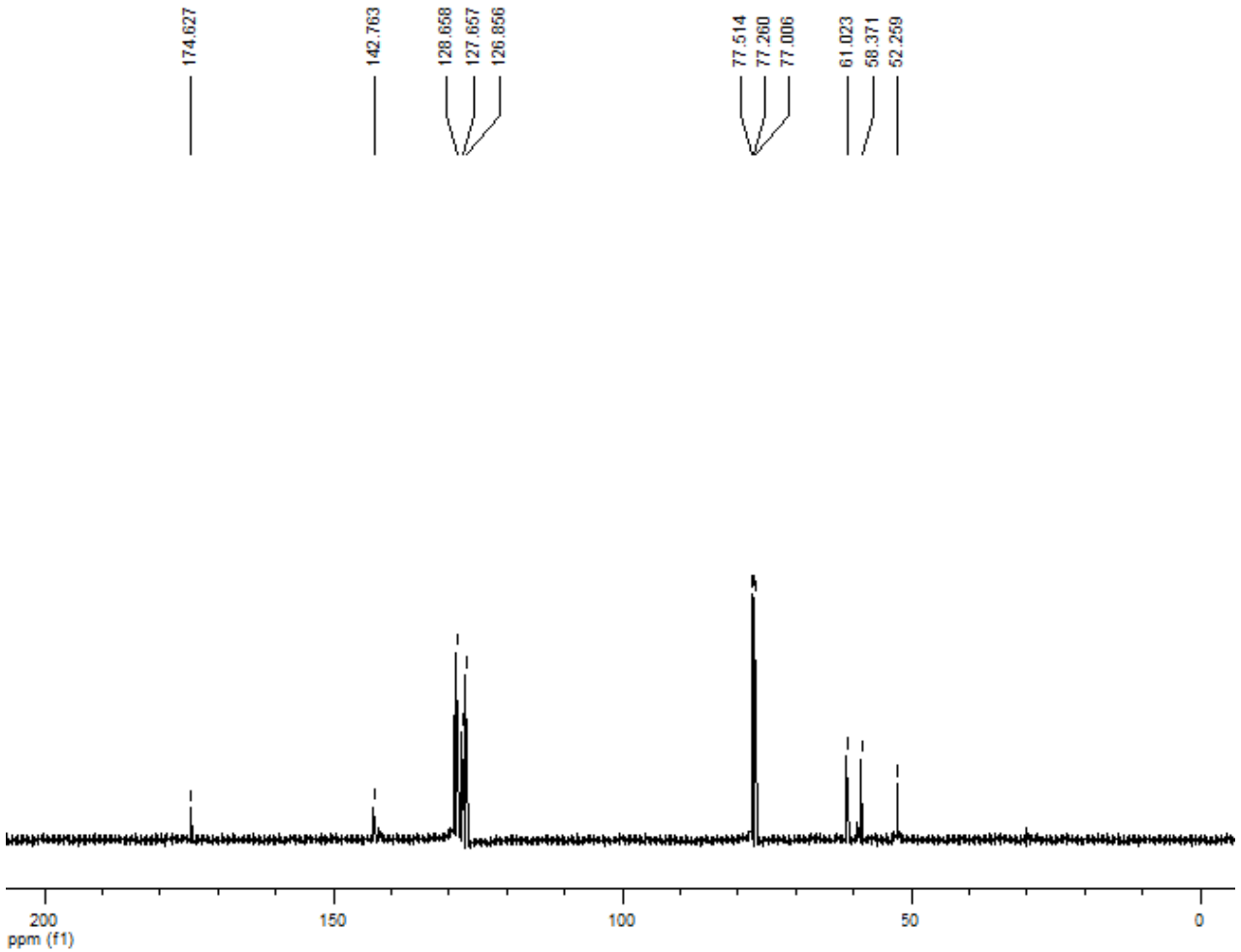

CO2Me
HCl·H2N
NH2·HCl
CF3

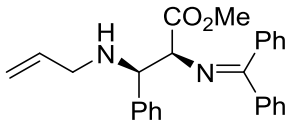
7c


2.05
0.90
1.19
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

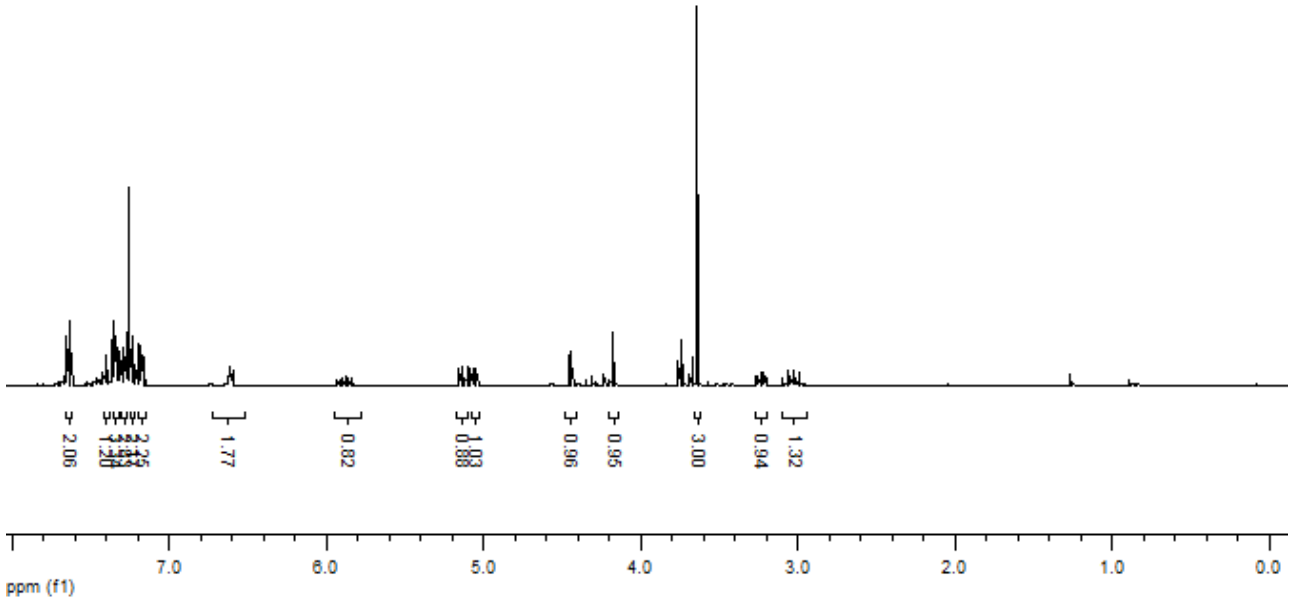

167.140
135.478
133.980
133.690
133.430
133.180
130.612
130.517
127.765
126.162
124.000
55.451
54.873
54.718
49.346
49.175
49.004
48.834
48.663
150
100
50
0

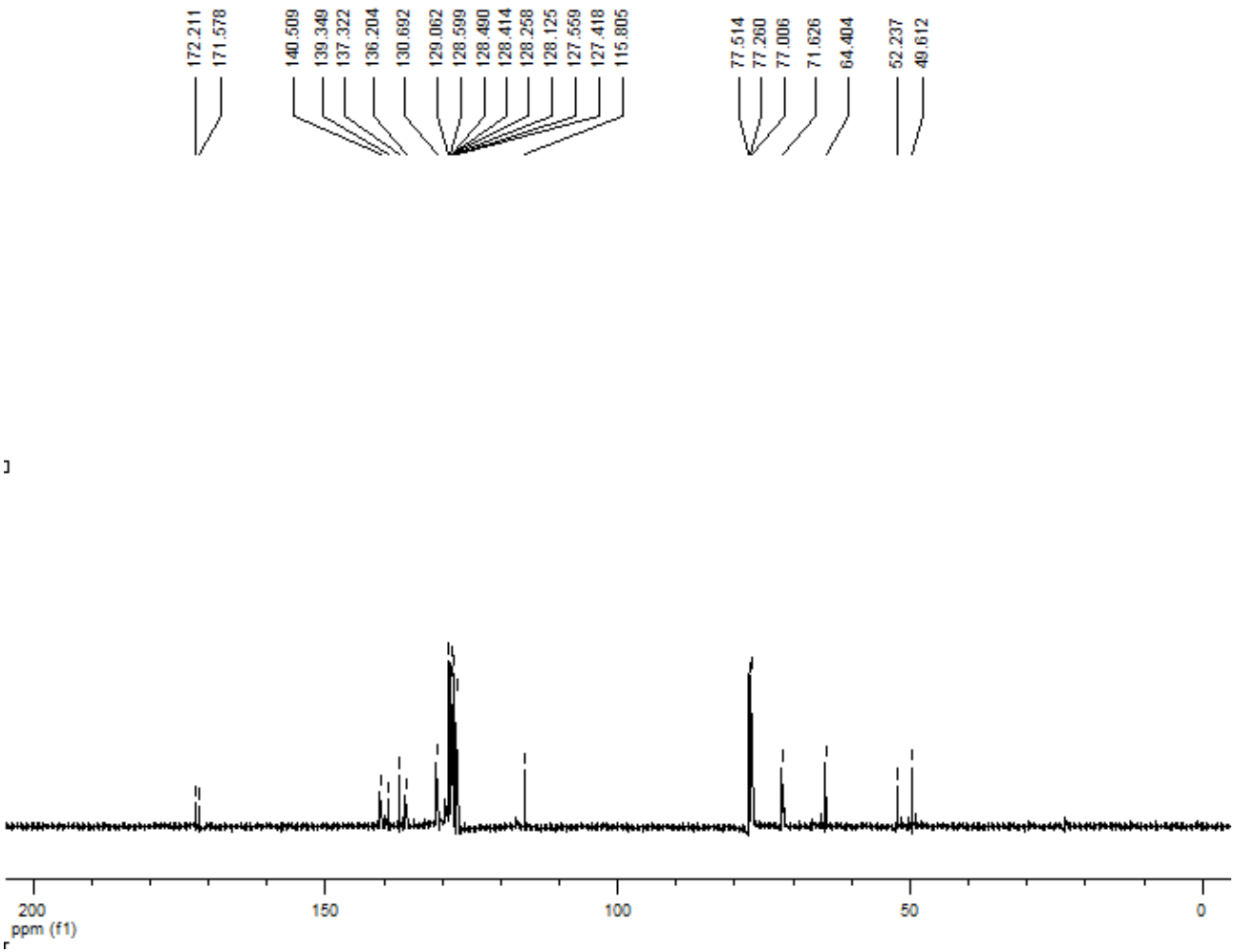

7.359
7.357
7.345
7.343
7.339
7.331
7.327
7.285
7.281
4.299
4.290
3.668
3.649
3.640
1.707
CO2Me
H2N
NH2
Ph
5.48
1.00
2.46
4.97
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

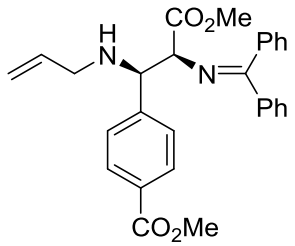

174.627
142.763
128.658
127.657
126.856
77.514
77.260
77.006
61.023
58.371
52.259
200
150
100
50
0
ppm (f1)


CO2Me
H
N
Ph
N
Ph
Ph

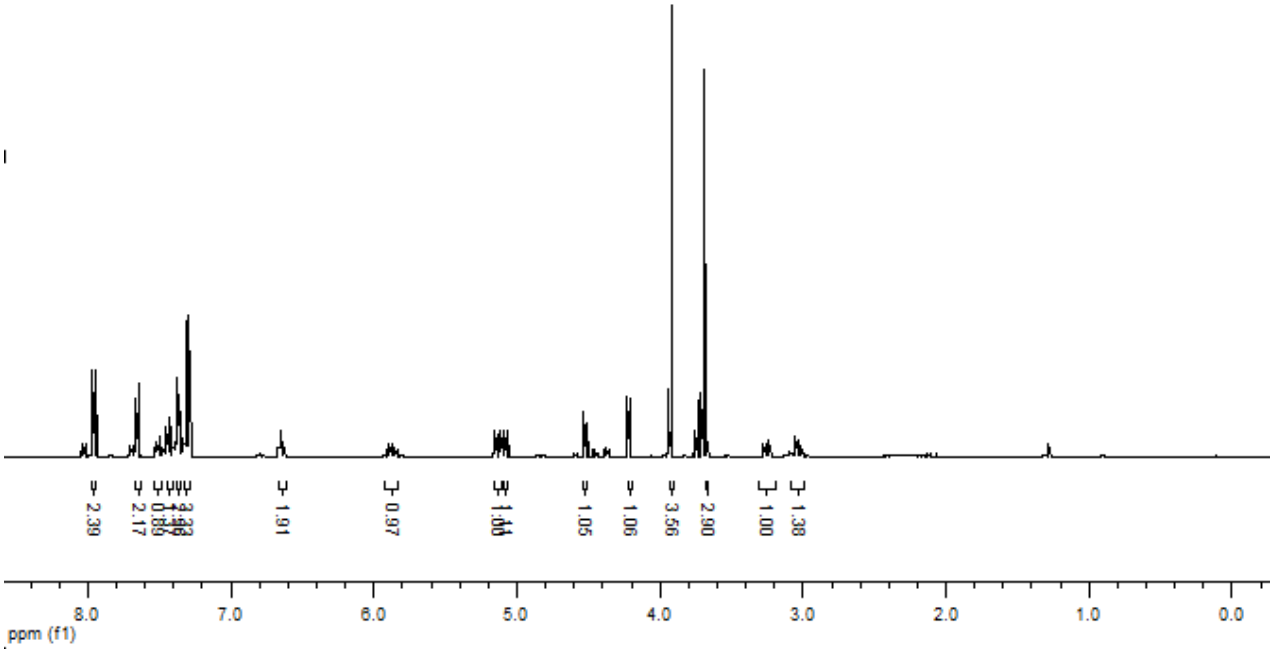
8a

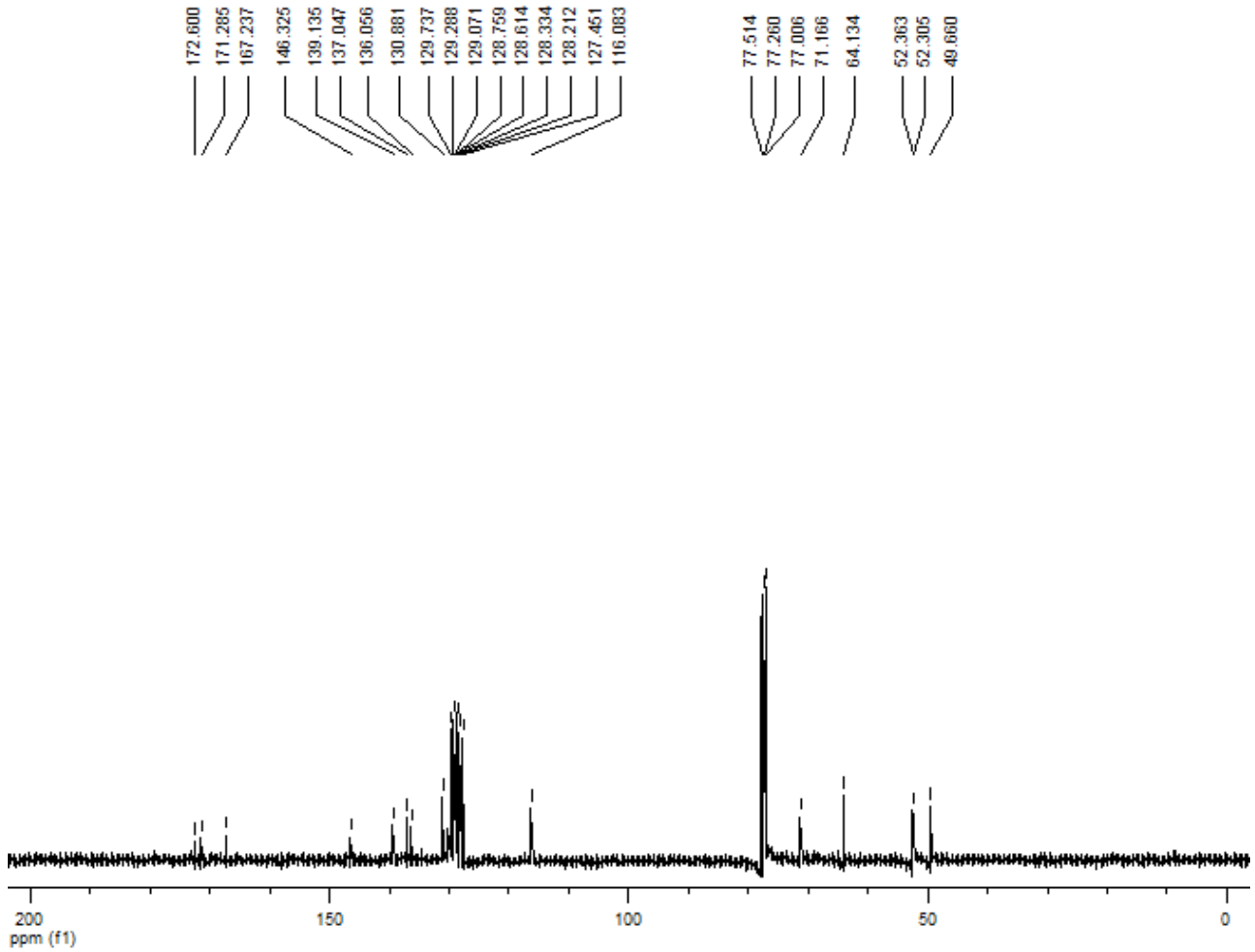

2.06
2.25
1.77
0.82
1.03
0.96
0.95
3.00
0.94
1.32
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

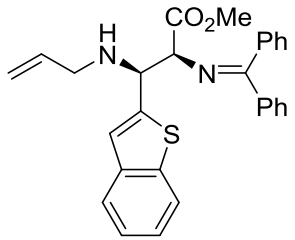

172.211
171.578
140.509
139.349
137.322
136.204
130.692
129.062
128.599
128.490
128.414
128.258
128.125
127.559
127.418
115.805
77.514
77.260
77.006
71.626
64.404
52.237
49.612
200
150
100
50
0
ppm (f1)


H
N
CO2Me
N
Ph
Ph
CO2Me

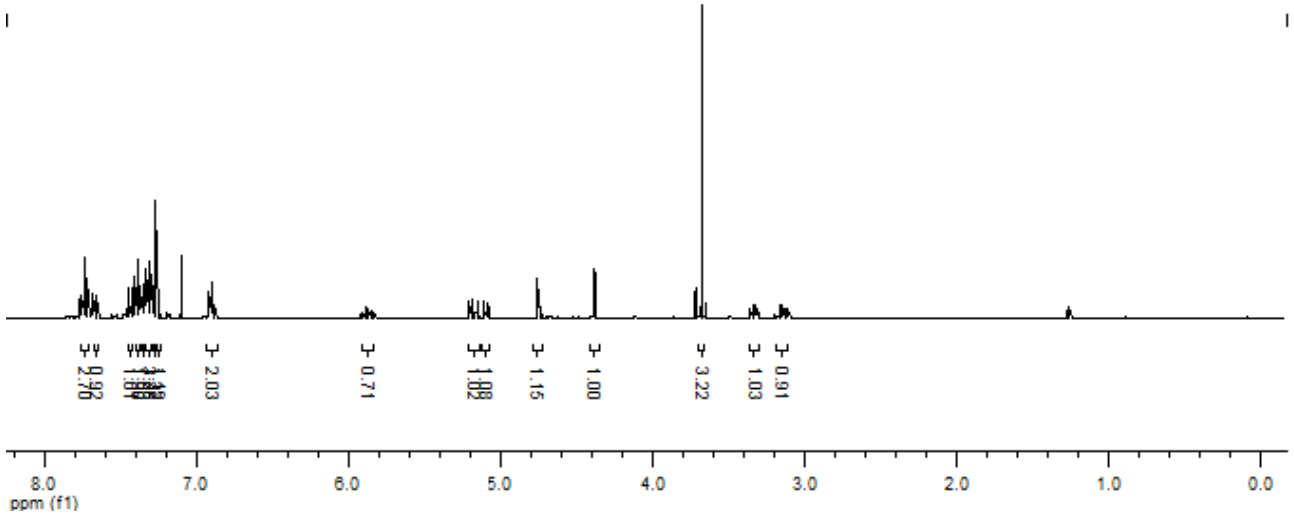
8b

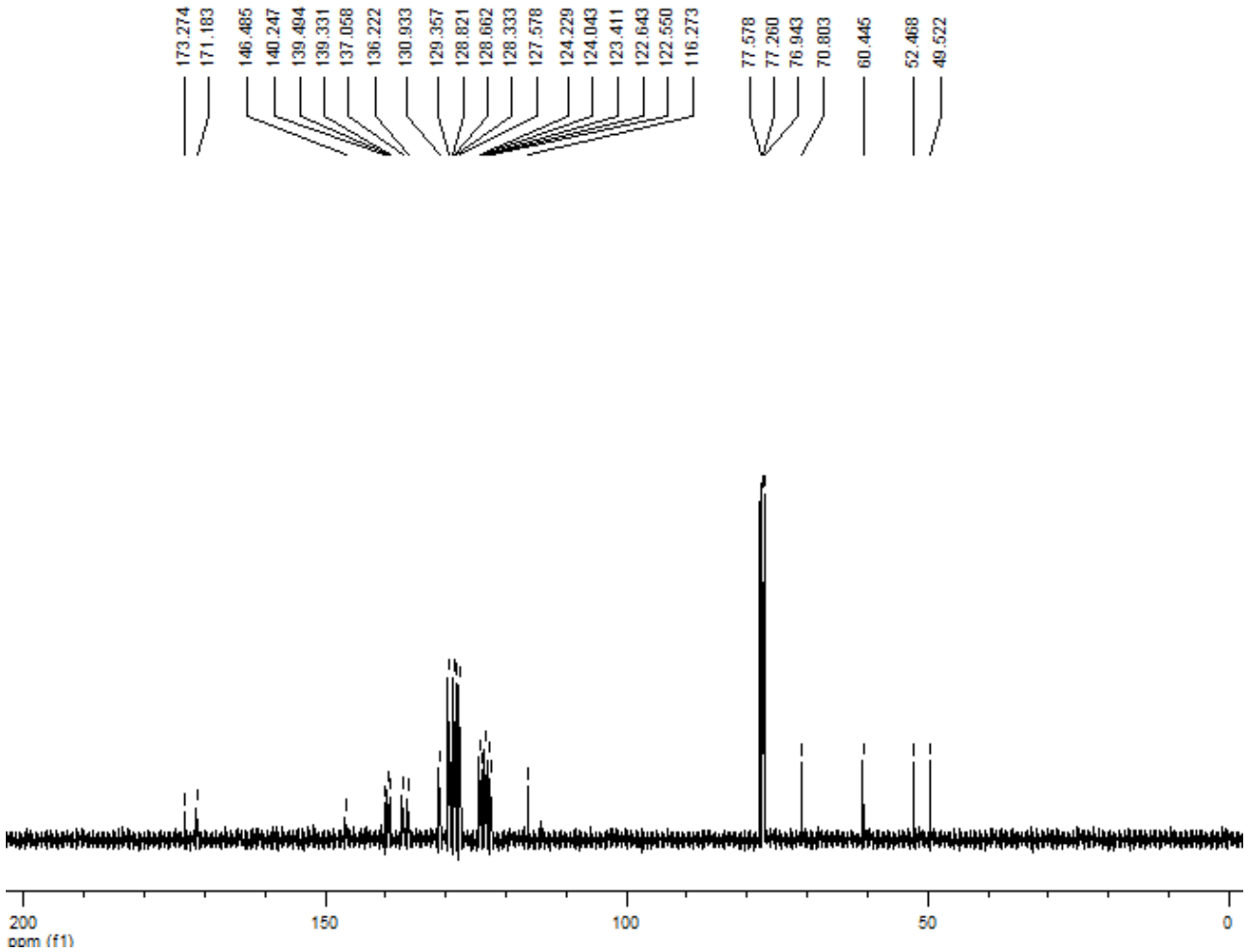

2.39
2.17
1.91
0.97
1.05
1.06
3.56
2.90
1.00
1.38
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

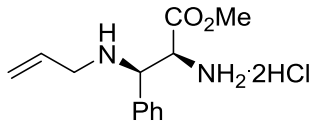

172.600
171.285
167.237
146.325
139.135
137.047
136.056
130.881
129.737
129.288
129.071
128.759
128.614
128.334
128.212
127.451
116.083
77.514
77.260
77.006
71.166
64.134
52.363
52.305
49.660
200
ppm (f1)
150
100
50
0


CO2Me
H
N
Ph
N
Ph
S

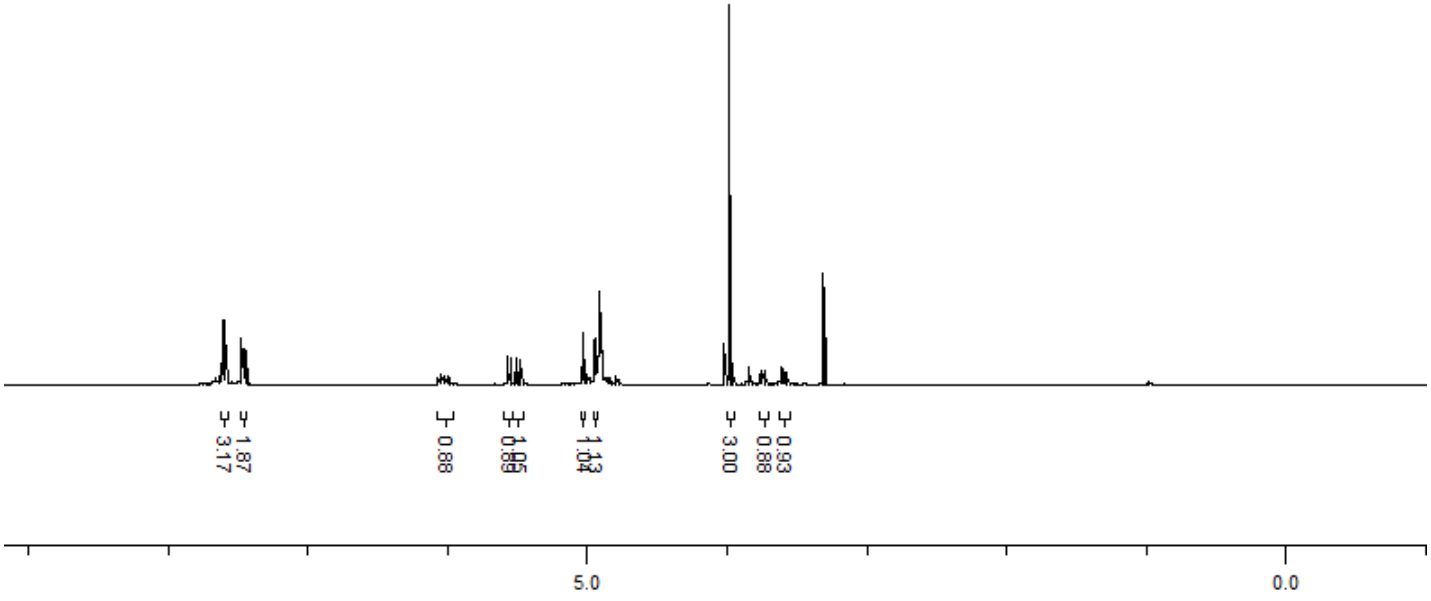
8c

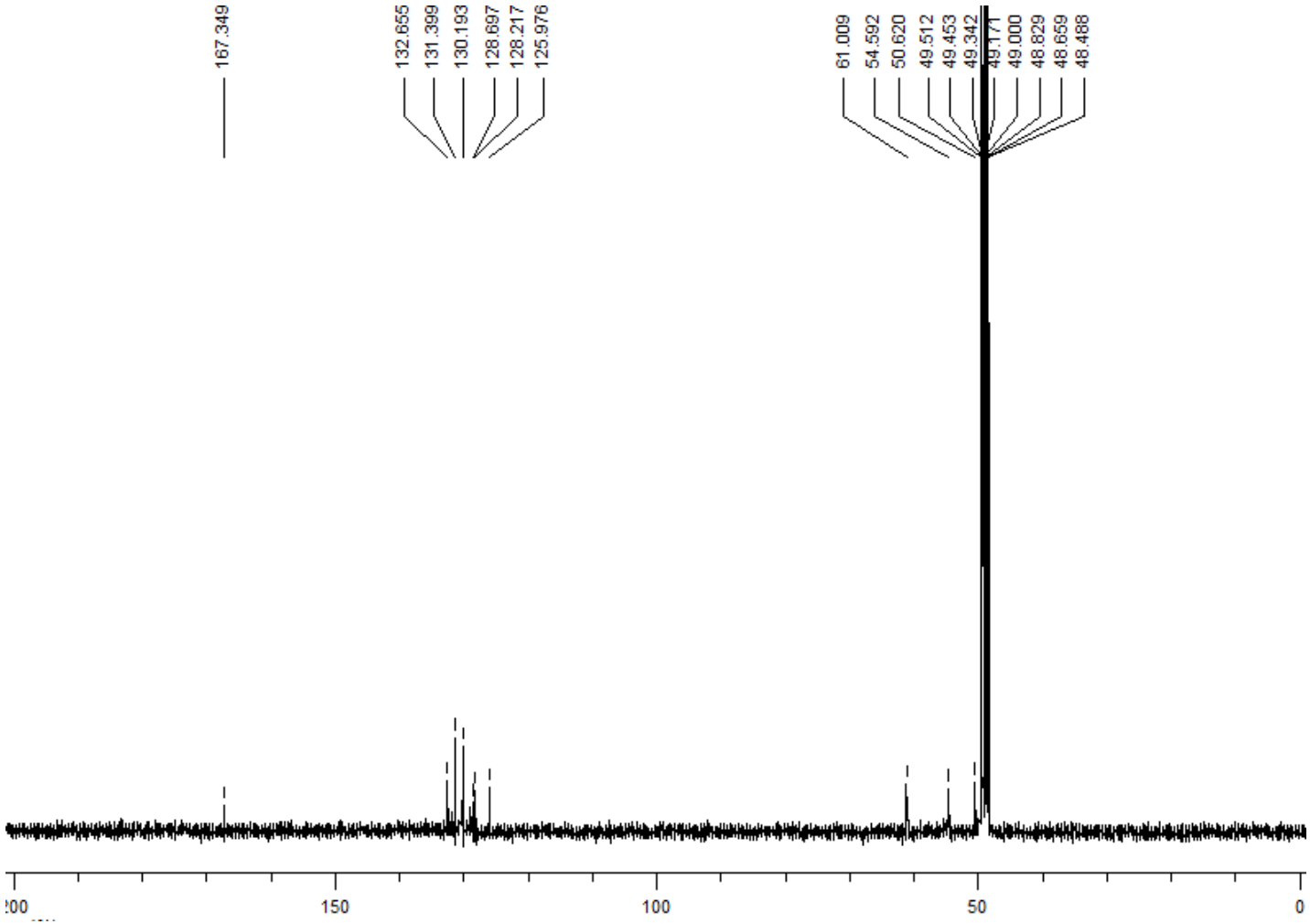

2.92
2.03
0.71
1.08
1.15
1.00
3.22
1.03
0.91
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

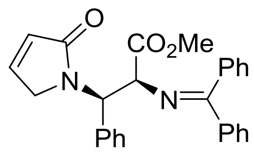

173.274
171.183
146.485
140.247
139.494
139.331
137.058
136.222
130.933
129.357
128.821
128.662
128.333
127.578
124.229
124.043
123.411
122.643
122.550
116.273
77.578
77.260
76.943
70.803
60.445
52.468
49.522
200
150
100
50
0
ppm (f1)


CO2Me
H
N
NH2·2HCl
Ph

9

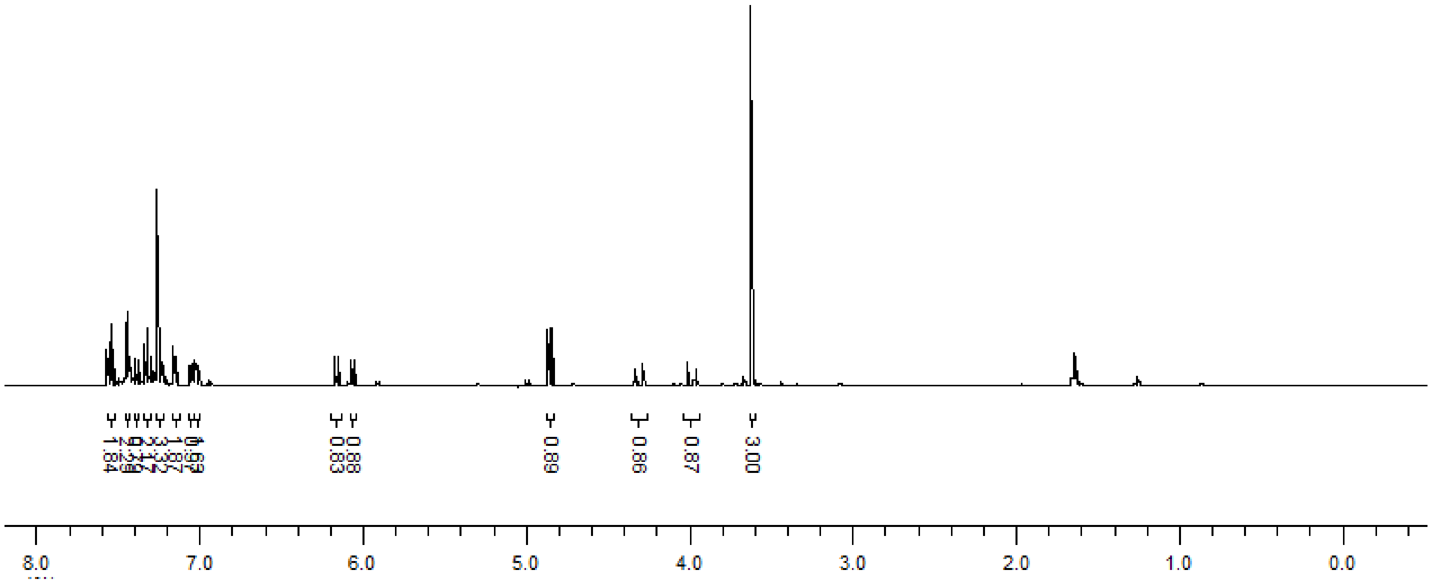

3.17
1.87
0.88
0.86
0.86
1.13
1.04
3.00
0.93
0.88
5.0
0.0


167.349
132.655
131.399
130.193
128.697
128.217
125.976
61.009
54.592
50.620
49.512
49.453
49.342
49.171
49.000
48.829
48.659
48.488
150
100
50
0

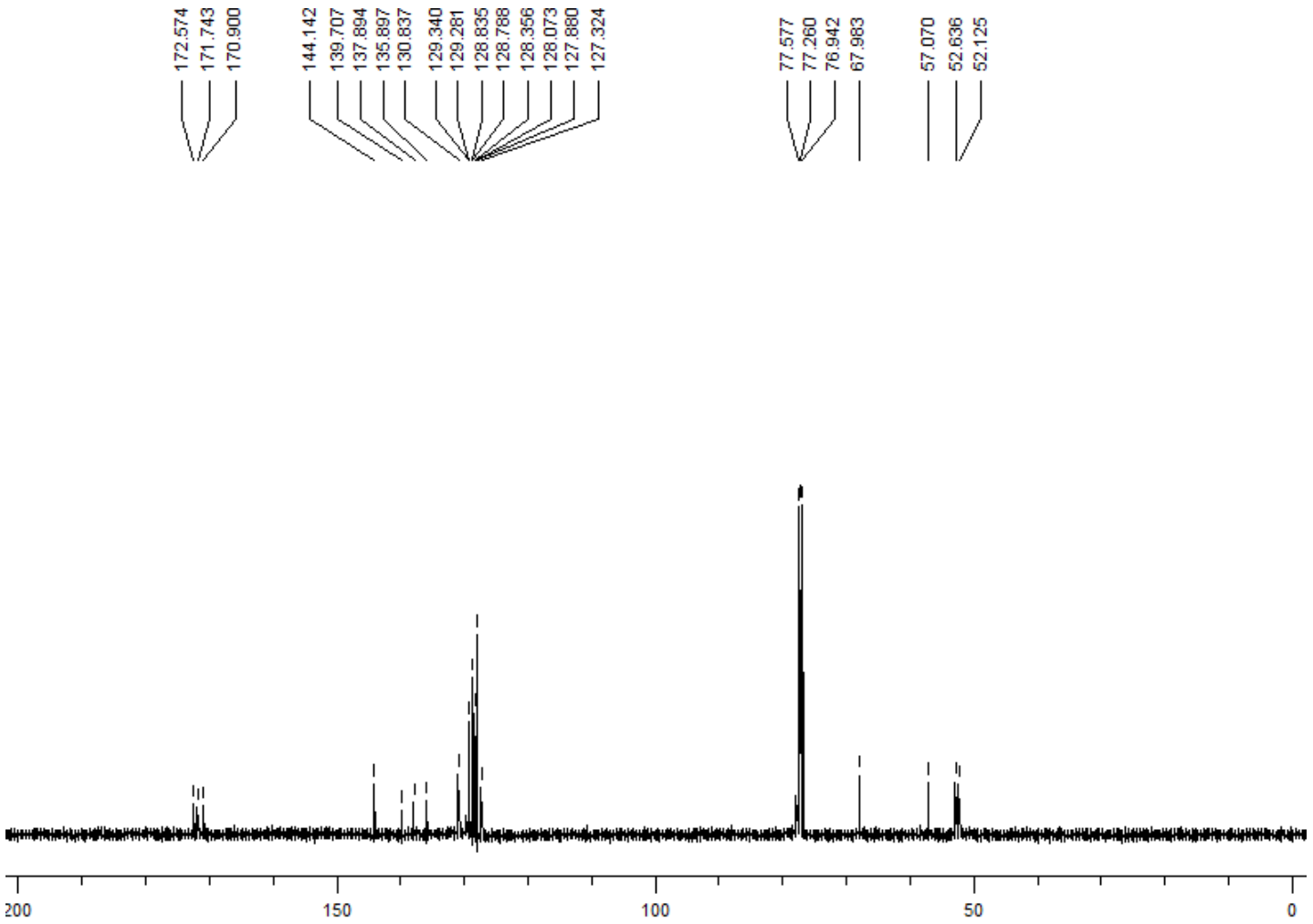


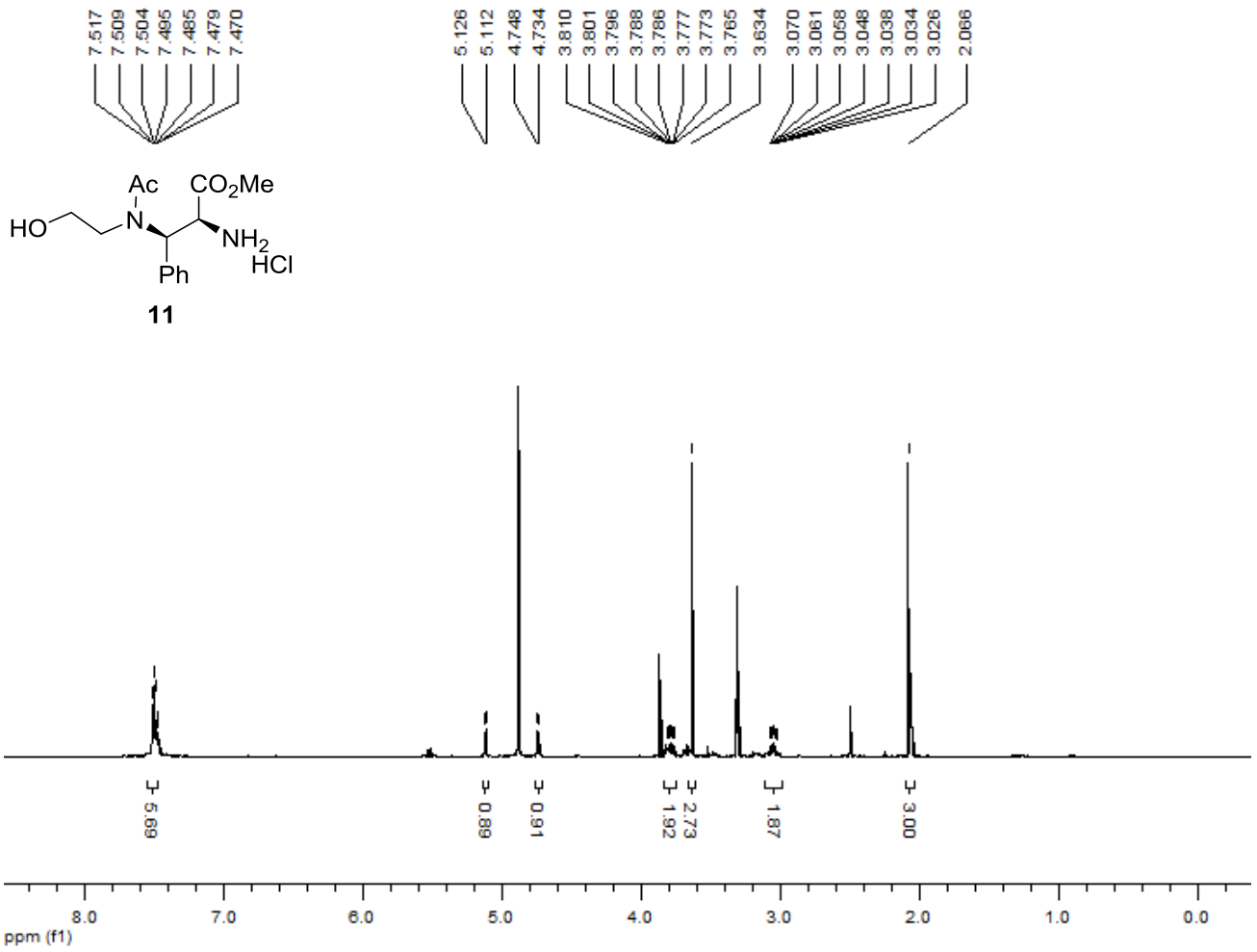
O
CO2Me
N
Ph
N
Ph
Ph

10

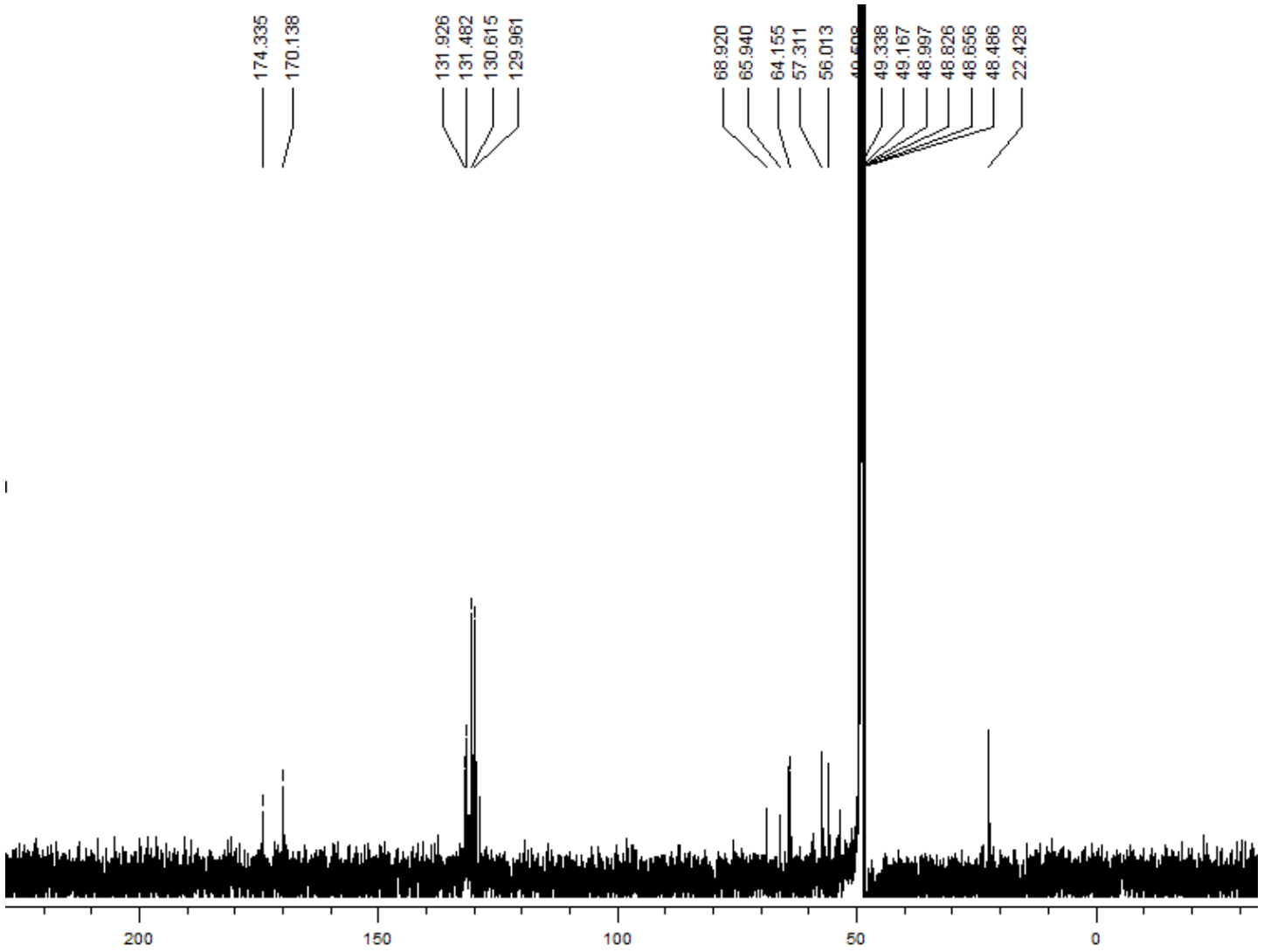


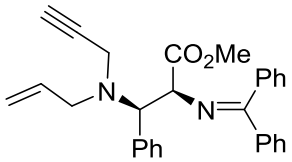
1.84
2.29
3.32
1.87
0.88
0.83
0.89
0.86
0.87
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0


172.574
171.743
170.900
144.142
139.707
137.894
135.897
130.837
129.340
129.281
128.835
128.788
128.356
128.073
127.880
127.324
77.577
77.260
76.942
67.983
57.070
52.636
52.125
200
150
100
50
0

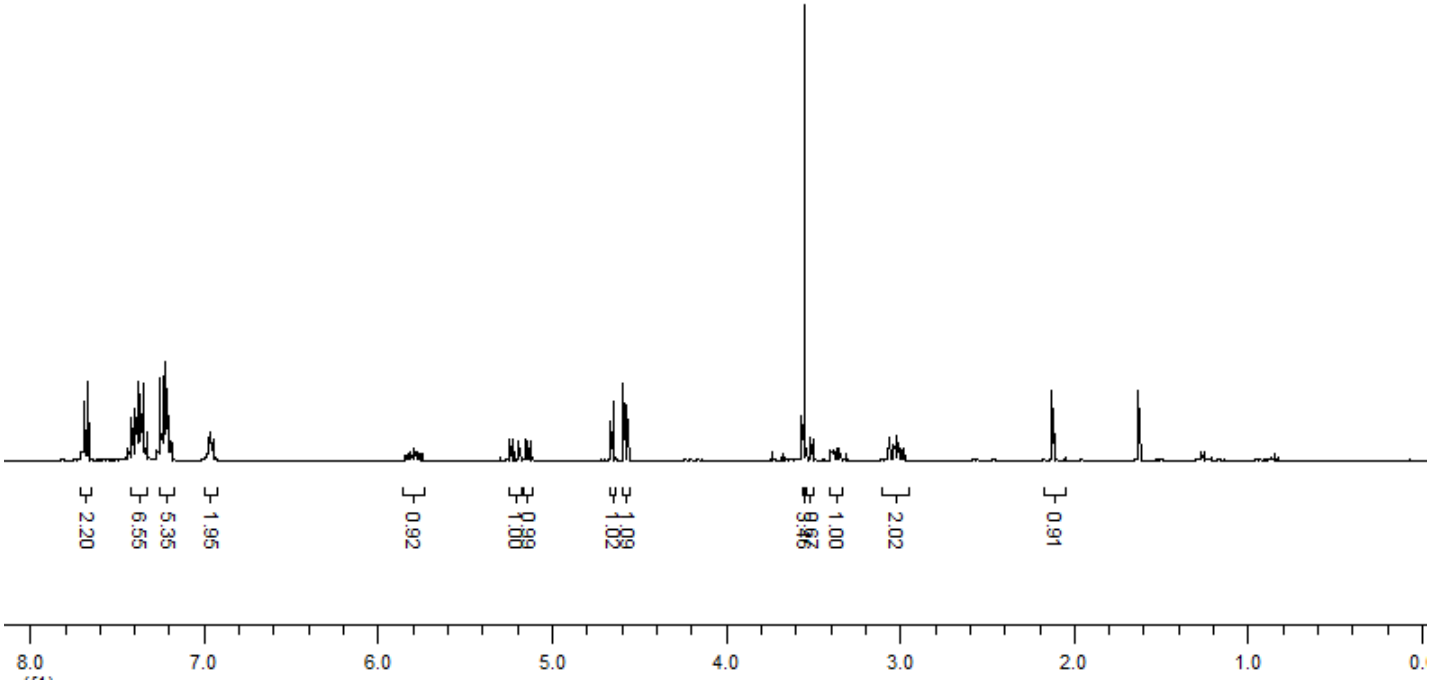

7.517
7.509
7.504
7.495
7.485
7.479
7.470
5.126
5.112
4.748
4.734
3.810
3.801
3.796
3.788
3.786
3.777
3.773
3.765
3.634
3.070
3.061
3.058
3.048
3.038
3.034
3.026
2.066
Ac
CO2Me
HO
N
NH2
HCl
Ph
5.69
0.89
0.91
1.92
2.73
1.87
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

11


174.335
170.138
131.926
131.482
130.615
129.961
68.920
65.940
64.155
57.311
56.013
49.338
49.167
48.997
48.826
48.656
48.486
22.428
200
150
100
50
0


CO2Me
Ph
N
N
Ph
Ph

12


2.20
6.55
5.35
1.95
0.92
0.99
1.00
1.02
1.00
2.02
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6.0
5.0
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2.0
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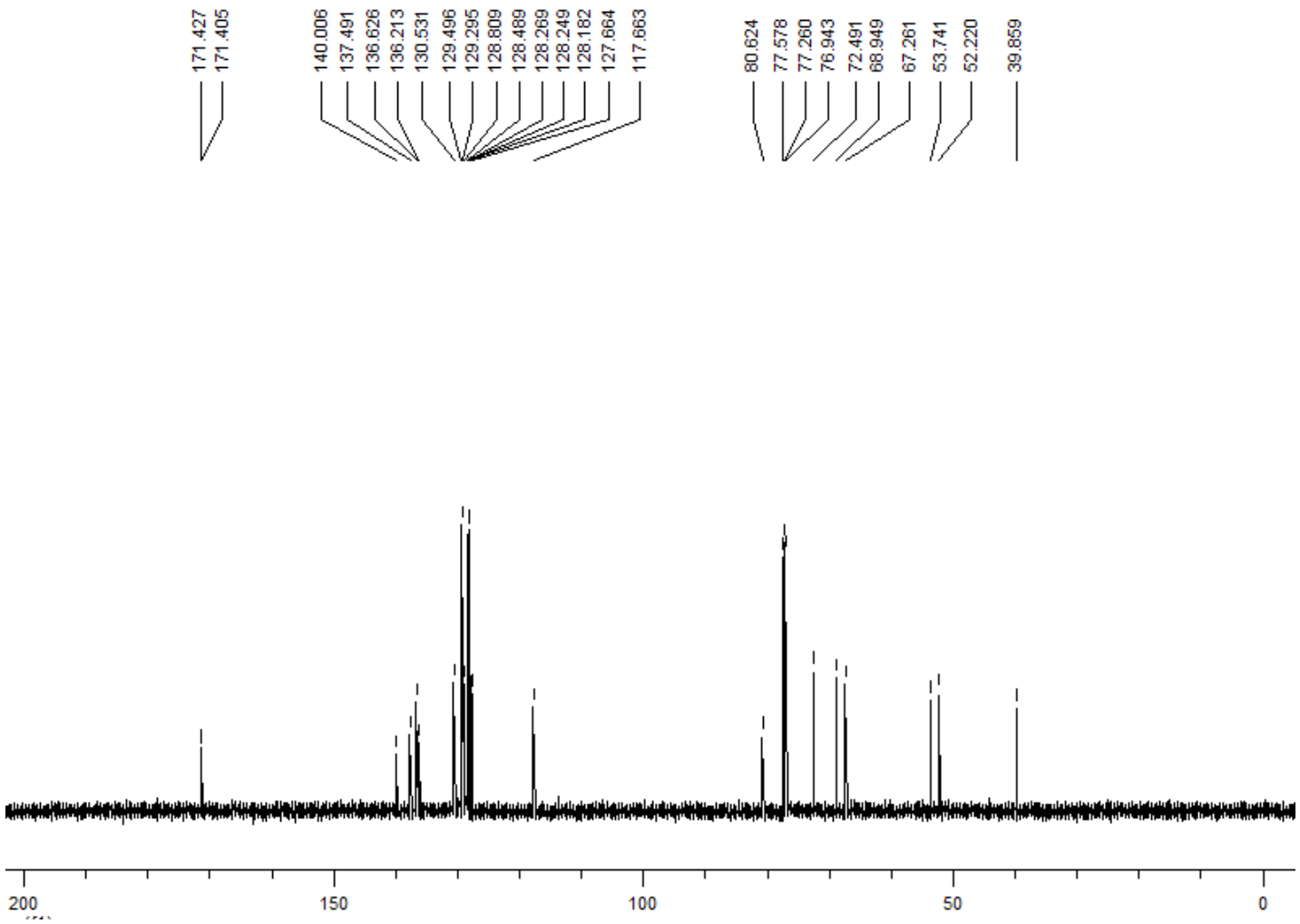
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171.405
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136.626
136.213
130.531
129.496
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128.489
128.269
128.249
128.182
127.664
117.663
80.624
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67.261
53.741
52.220
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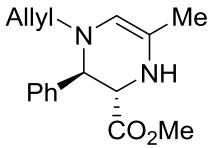
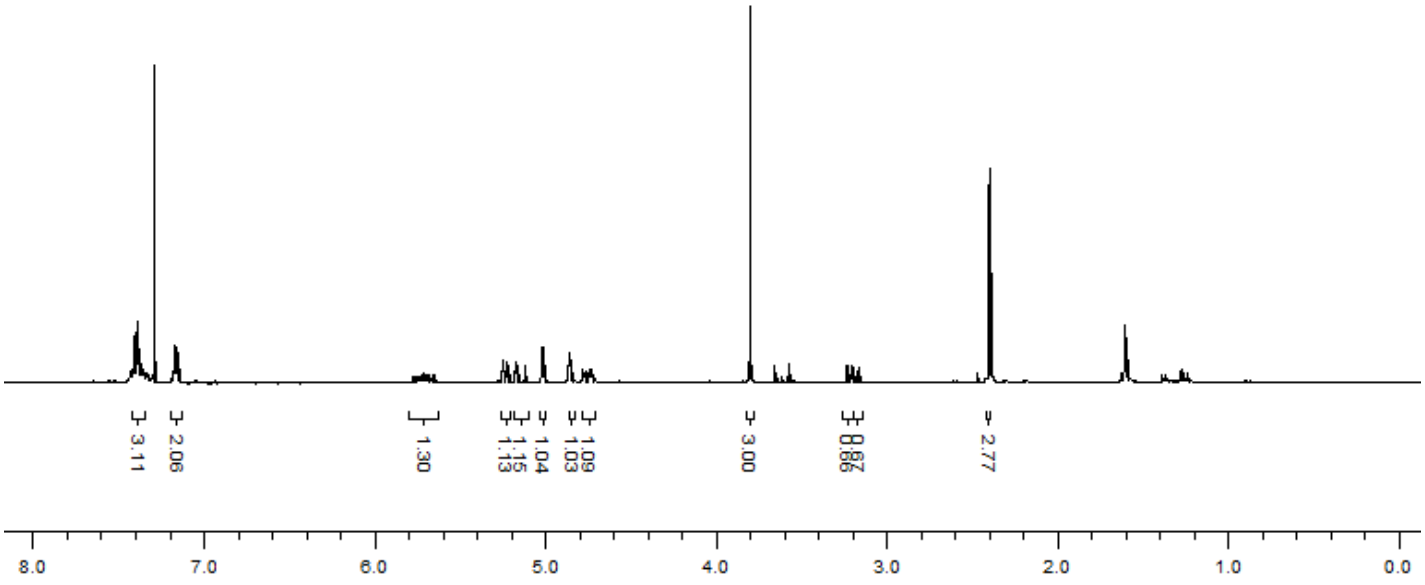

Allyl
N
Me
NH
Ph
CO2Me

13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2.06
1.30
1.15
1.13
1.04
1.09
1.03
3.00
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2.77
8.0
7.0
6.0
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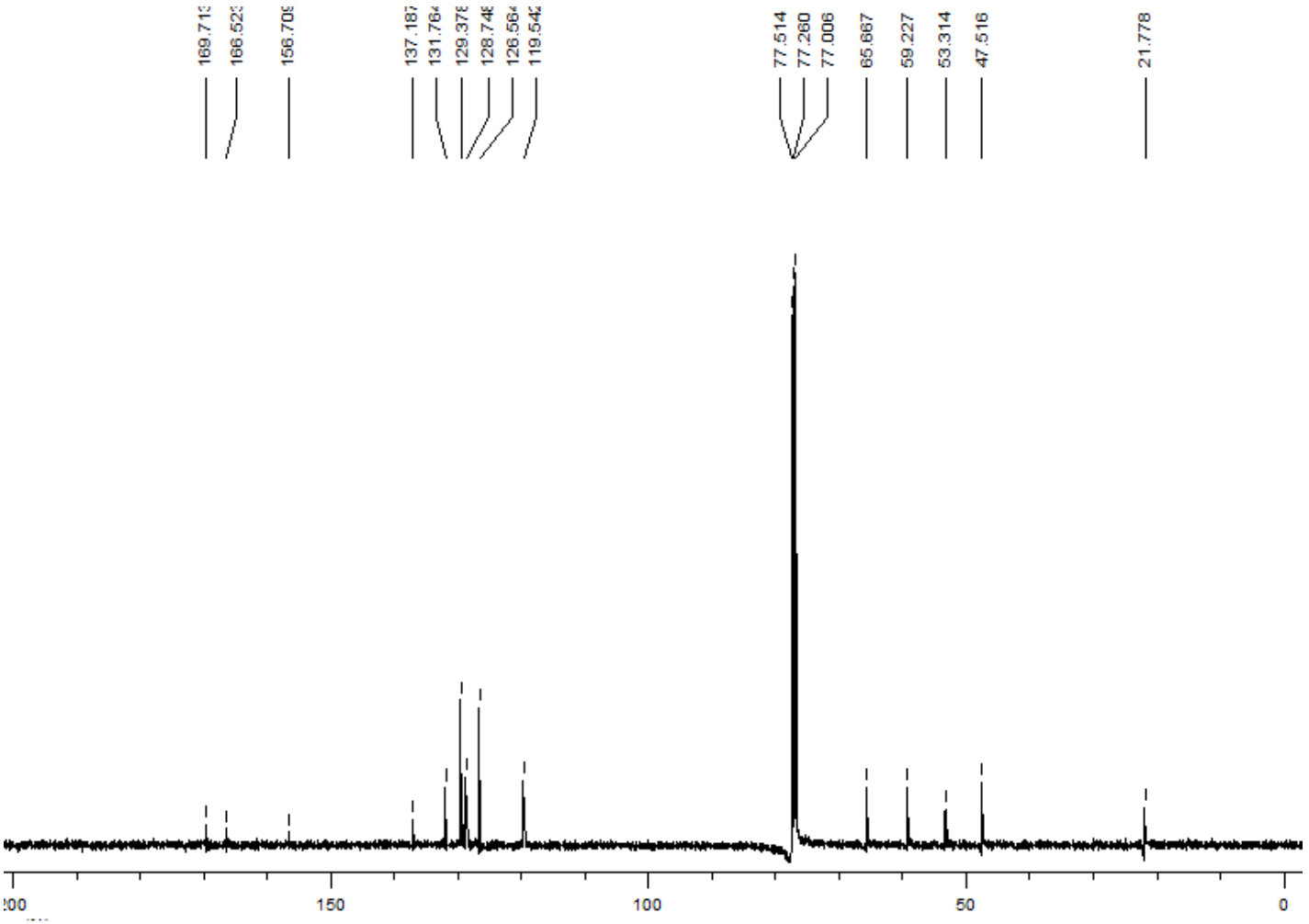
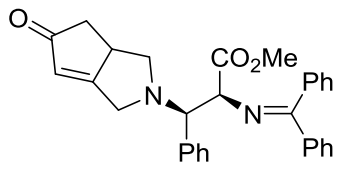
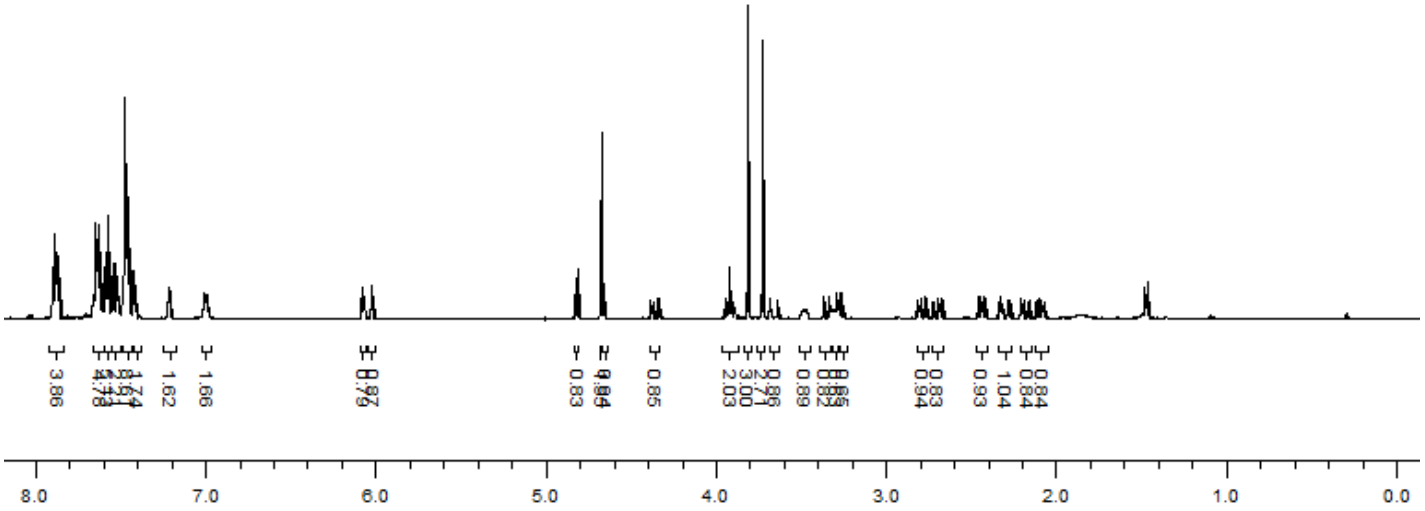
4.0
3.0
2.0
1.0
0.0


169.71
166.52
156.70
137.18
131.76
129.37
128.74
126.56
119.54
77.514
77.260
77.006
65.667
59.227
53.314
47.516
21.778
150
100
50
0


O
CO2Me
Ph
N
N
Ph
Ph

14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1.62
1.66
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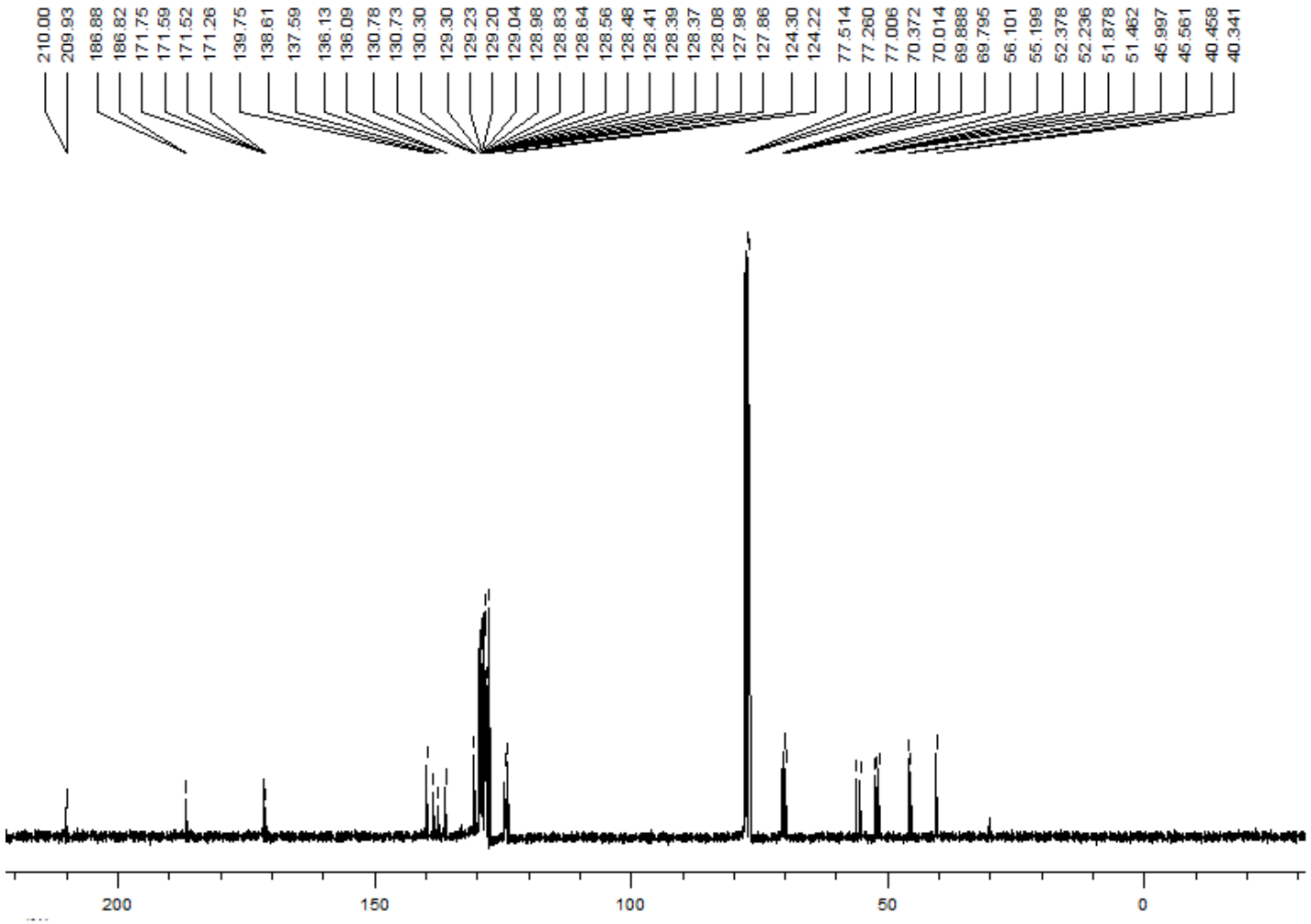
0.85
2.03
3.00
0.89
0.94
0.93
1.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0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186.88
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136.13
136.09
130.78
130.73
130.30
129.30
129.23
129.20
129.04
128.98
128.83
128.64
128.56
128.48
128.41
128.39
128.37
128.08
127.98
127.86
124.30
124.22
77.514
77.260
77.006
70.372
70.014
69.888
69.795
56.101
55.199
52.378
52.236
51.878
51.462
45.997
45.561
40.458
40.341
200
150
100
50
0