Supporting Information for:

Enantioselective γ-Borylation of Unsaturated Amides and Stereoretentive Suzuki-Miyaura Cross-Coupling

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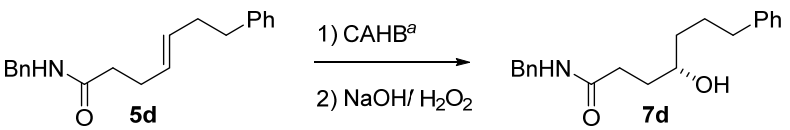
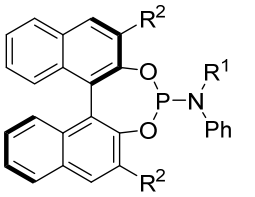
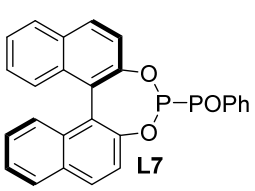
General procedures. Reactions were carried out in a dry nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled under sodium metal and benzophenone. HPLC solvents were filtered through Millipore filter paper. 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinBH) was distilled immediately before use. All synthesized compounds were purified with flash chromatography using EMD Silica Gel 60 Geduran®, distilled via short path distillation, or triturated. Thin Layer Chromatography analyses were performed on Analtech Silica Gel HLF (0.25 mm) precoated analytical plates and visualized with use of handheld short wavelength UV light, Iodine stain (I_2 and EMD Silica Gel 60 Geduran®) and Vanillin stain (Ethanol, H_2SO_4, and vanillin). HPLC analyses were performed with use of an ISCO model 2360 HPLC and Chiral Technologies, Inc. chiral HPLC columns (Chiralcel-OJ-H, column: 250 x 4.6 mm; Chiralcel-OD, column: 250 x 4.6 mm; Chiralpak-IC, column: 250 x 4.6 mm; (*S,S*)-WHELK-O 1, column: 250 x 4.6 mm) and monitored with UV-VIS detector (Shimadzu SPD-10A$_{VP}$/10A$_{VP}$, $\lambda = 210$ nm). Data were recorded and analyzed with ChromPerfect chromatography software (version 5.1.0). NMR spectra were recorded on 400 MHz and 300 MHz Bruker Advance NMR spectrometers using residue $CHCl_3$ (δ 7.27 ppm) or $CDCl_3$ (δ 77.0 ppm) for reference unless otherwise specified. Peaks are expressed as m (unresolved multiplet), q (quartet), t (triplet), d (doublet) or s (singlet). IR spectra were recorded using an Avatar 360 FT-IR. Optical rotations were measured as solutions, 1.0 g/100 mL in chloroform or methanol unless indicated otherwise, and recorded using an Autopol III automatic polarimeter. HRMS analyses were performed by the Nebraska Center for Mass Spectrometry. Ligands **L1** and **L2** and Buchwald cataCXium® A Pd G3 (**20**) precatalyst are prepared as previously reported.[1]

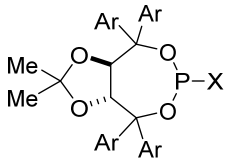




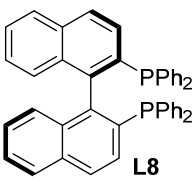
L1: R^1 = Me, R^2 = H
L2: R^1 = Bn, R^2 = H
L3: R^1 = Bn, R^2 = Me
L4: R^1 = Bn, R^2 = Et
L5: R^1 = Bn, R^2 = CF_3
L6: R^1 = Bn, R^2 = $SiMe_3$



L7



Ar = 3,5-$Me_2C_6H_3$
L9: X = N(Me)Ph
L10: X = OPh



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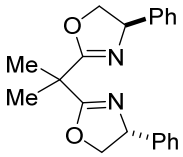

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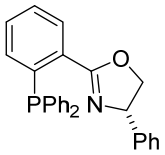
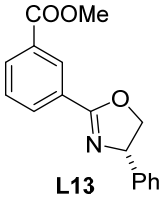
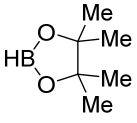


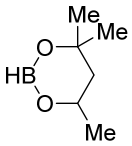
L12



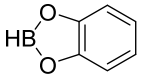
L13



B1: pinBH



B2: tmdBH

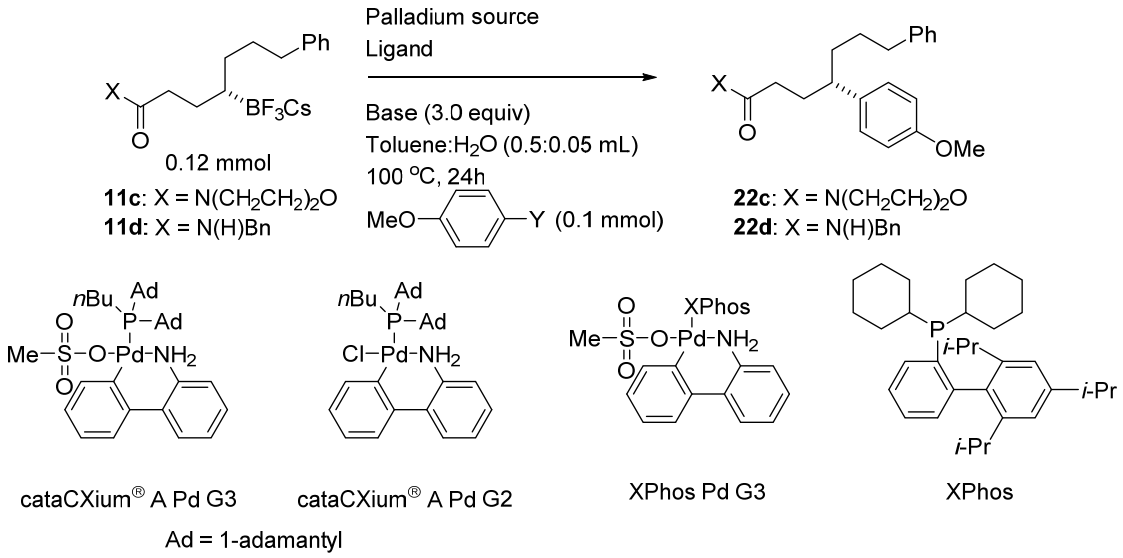


B3: catBH

	B1 (pinBH)				**B2** (tmdBH)				**B3** (catBH)			
Ligand	Entry	**5d**	**7d**	% ee	Entry	**5d**	**7d**	% ee	Entry	**5d**	**7d**	% ee
L1	1	0	91	93	14	80	12	n.d.	27	0	81	37
L2	2	0	95	90	15	60	15	n.d.	28	0	83	30
L3	3	0	64	87	16	35	0	n.d.	29	–		
L4	4	0	52	85	17	27	5	n.d.	30	–		
L5	5	0	19	85	18	11	0	n.d.	31	–		
L6	6	0	90	90	19	70	10	n.d.	32	–		
L7	7	80	0	n.d.	20	>90	0	n.d.	33	0	60	n.d.
L8	8	84	0	n.d.	21	>90	0	n.d.	34	30	57	n.d.
L9	9	0	70	–43[b]	22	>90	0	n.d.	35	18	69	–8[b]
L10	10	0	85	46	23	>90	0	n.d.	36	10	76	48
L11	11	0	14	n.d.	24	>90	0	n.d.	37	0	40	n.d.
L12	12	50	17	n.d.	25	80	11	n.d.	38	22	67	–16[c]
L13	13	0	24	n.d.	26	75	0	n.d.	39	6	36	n.d.

*[a] CAHB conditions: 0.0528 mmol **5d**, 1.0 mol% $Rh(nbd)_2BF_4$, 1.0 mol% bidentate ligand or 2.0 mol% monodentate ligand, 1.5 equiv. borane, THF (C = 0.106 M), 40 °C, 5h; yield was reported as crude ^1H NMR yield using mesitylene as an internal standard and an average of two experiments generally exhibiting a spread of ±2%; %ee was determined by chiral HPLC Chiralpak-IC column (HPLC conditions vide infra); n.d. = not determined. [b] Enantioswithching observed when using (R)-**L9**. [c] (S)-**L12** was used.*

Table S1. Optimization studies for CAHB of **5d**

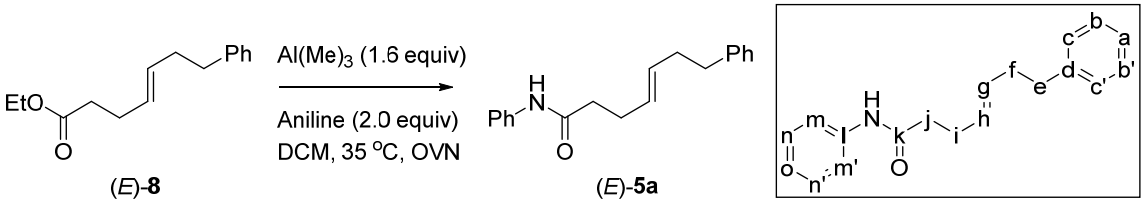


Entry	Pd source	Ligand	Base	Y	**22c** (%)	**22d** (%)
1	$Pd(OAc)_2$	XPhos	K_2CO_3	Cl	0	0
2	$Pd_2(dba)_3$	XPhos	K_2CO_3	Cl	38	0
3	$Pd_2(dba)_3$	P(*t*Bu)$_3$.HBF_4	K_2CO_3	Cl	10	0
4	$Pd_2(dba)_3$	cataCXium® A	K_2CO_3	Cl	15	0
5	XPhos Pd G3	–	K_2CO_3	Cl	21	0
6	cataCXium® A Pd G2	–	K_2CO_3	Cl	49	0
7	cataCXium® A Pd G3	–	K_2CO_3	Cl	52	0
8[a]	cataCXium® A Pd G3	cataCXium® A	K_2CO_3	Cl	45	0
9	cataCXium® A Pd G3	–	Cs_2CO_3	Cl	50	0
10	cataCXium® A Pd G3	–	K_3PO_4	Cl	47	0
11	cataCXium® A Pd G3	–	CsOH	Cl	0	0
12	cataCXium® A Pd G3	–	K_2CO_3	Br	45	0
13	cataCXium® A Pd G3	–	Cs_2CO_3	Br	42	0
14[b]	cataCXium® A Pd G3	–	K_2CO_3	Cl	48	0
15[c]	cataCXium® A Pd G3	–	K_2CO_3	Cl	0	0
16[c]	cataCXium® A Pd G3	–	Cs_2CO_3	Cl	0	0

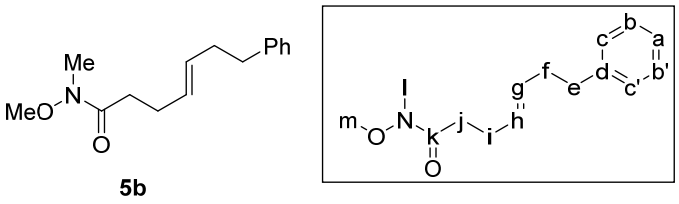
General conditions: 7.5 mol% Pd-precatalyst or 10 mol% $Pd(OAc)_2$ or 5 mol% $Pd_2(dba)_3$; 20 mol% ligand; isolated yield. [a] *Additional 7.5 mol%* cataCXium® A. [b] *Toluene:H_2O = 0.25:0.25 mL.* [c] *Bpin is used instead of BF_3Cs.*

Table S2. Optimization studies for Suzuki-Miyaura cross-couplings of **11c–d**

General procedure for the preparation of (*E*)-γ,δ-unsaturated amides via trimethylaluminum mediated amide bond formation (GP1)

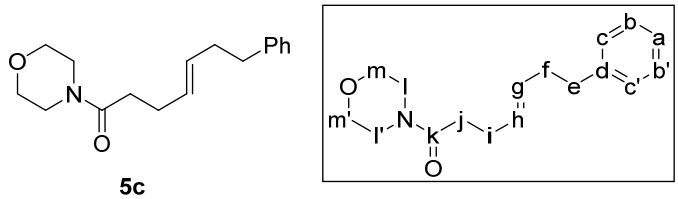


Prepration of (*E*)-7-phenyl-4-heptenecarboxylic acid phenyl amide ((*E*)-5a). To a solution of aniline (2 equiv, 10 mmol, 0.91 mL) in DCM (20 mL) was slowly added trimethylaluminum (1.62 equiv, 2.0 M in hexanes, 8.1 mmol, 4.05 mL) at room temperature. The resulting mixture was stirred at room temp for 30 mins, and the corresponding ethyl ester ((*E*)-7-phenyl-4-heptenecarboxylic acid ethyl ester **(*E*)-8**, 5 mmol, 1.16g) was added dropwise. The resultant mixture was heated overnight at 35 °C. After cooling to room temperature, the reaction mixture was quenched with HCl (1M) and extracted with DCM (3 x 20 mL). The combined organic extracts were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate) affords the title compound (992 mg, 71%) as a white solid: m.p. 106.0–107.0 °C; TLC analysis R_f 0.65 (60:40 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (2H, d, *J* = 7.8 Hz, m,m'), 7.48 (1H, br s, NH), 7.25–7.40 (4H, m, b,b',n,n'), 7.15–7.25 (3H, m, c,c',a), 7.13 (1H, t, *J* = 7.4 Hz, o), 5.40–5.70 (2H, m, g,h), 2.70 (2H, t, *J* = 7.4 Hz, e), 2.25–2.50 (6H, m, f,i,j); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.03 (k), 142.00 (d), 138.06 (l), 131.30 (h), 129.10 (g), 129.05 (n,n'), 128.61 (b,b'), 128.40 (o), 125.92 (c,c'), 124.36 (a), 120.07 (m,m'), 37.65 (e), 36.01 (j), 34.44 (f), 28.60 (i); IR (neat) 3305 (N-H stretch), 3265, 2193, 1664 (C=O stretch), 1603, 1546, 1439, 972, 757, 693 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{21}NNaO$ (M+Na): 302.1521, found 302.1531 *m/z*.



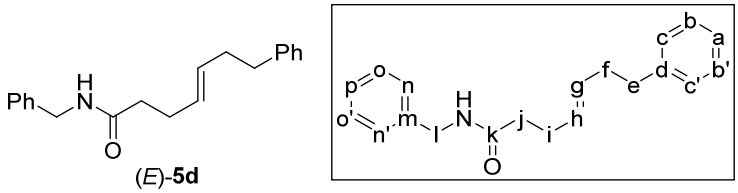
(*E*)-7-phenyl-4-heptenecarboxylic acid Weinreb amide (5b). Following **GP1** with *N*-methoxy-*N*-methylamine hydrochloride (5 equiv, 25 mmol, 2.4 g) and trimethylaluminum (5

equiv, 2.0 M in hexanes, 25 mmol, 12.5 mL) affords, after flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate), the title compound (780 mg, 63%) as a yellow oil; TLC analysis R_f 0.5 (60:40 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.35 (2H, m, b,b'), 7.15–7.25 (3H, m, a,c,c'), 5.45–5.65 (2H, m, g,h), 3.69 (3H, s, m), 3.20 (3H, s, l), 2.69 (2H, t, *J* = 7.4 Hz, e), 2.49 (2H, m, j), 2.20–2.40 (4H, m, f,i); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.14 (k), 142.16 (d), 130.50 (h), 129.63 (g), 128.59 (b,b'), 128.35 (c,c'), 125.84 (a), 61.33 (m), 36.10 (e), 34.50 (f), 32.30 (l), 32.01 (j), 27.65 (i) ; IR (neat) 2934 (C-H sp^3 stretch), 1661 (C=O stretch), 1452, 1413, 1383 (C-N stretch), 969, 698 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{21}NNaO_2$ (M+Na): 270.1470, found 270.1469 *m/z*.



5c

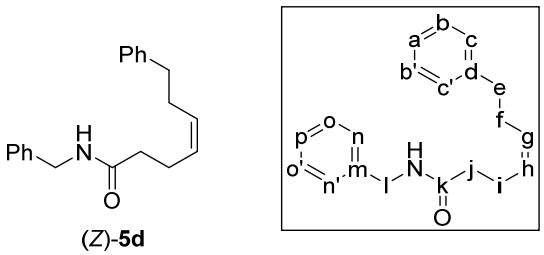
(*E*)-7-phenyl-4-heptenecarboxylic acid morpholino amide (5c). Following **GP1** with morpholine (2 equiv, 10 mmol, 0.87 mL) affords, after flash chromatography on silica gel (70:30-50:50 hexanes:ethyl acetate), the title compound (1.03 g, 75%) as a yellow oil; TLC analysis R_f 0.4 (40:60 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.35 (2H, m, b,b'), 7.15–7.25 (3H, m, a,c,c'), 5.40–5.60 (2H, m, g,h), 3.55–3.70 (6H, m, l,l',m,m'), 3.35–3.50 (2H, m, l,l'), 2.68 (2H, t, *J* = 7.5 Hz, e), 2.20–2.40 (6H, m, f,i,j); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.23 (k), 142.05 (d), 131.68 (h), 129.47 (g), 128.59 (b,b'), 128.36 (c,c'), 125.87 (a), 67.05 and 66.76 (m,m'), 46.08 and 42.01 (l,l'), 36.04 (e), 34.46 (f), 33.13 (j), 28.28 (i); IR (neat) 2914 (C-H sp^3 stretch), 2852, 1642 (C=O stretch), 1428, 1113, 968, 699 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{23}NNaO_2$ (M+Na): 296.1626, found 296.1628 *m/z*.



(*E*)-**5d**

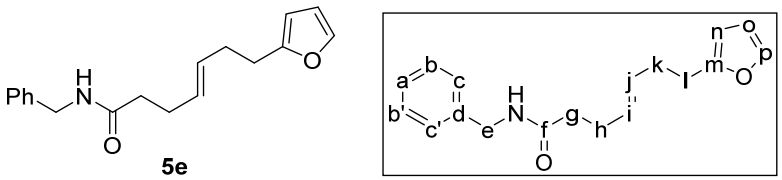
(*E*)-7-phenyl-4-heptenecarboxylic acid benzyl amide ((*E*)-5e). Following **GP1** with benzyl amine (2 equiv, 10 mmol, 1.1 mL) affords, after flash chromatography on silica gel (80:20-

60:40 hexanes:ethyl acetate), the title compound (1.15 g, 78%) as a white solid: m.p. 65.5–66.5 °C; TLC analysis R_f 0.4 (60:40 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.40 (10H, m, a,b,b',c,c',n,n',o,o',p), 5.89 (1H, br s, NH), 5.40–5.60 (2H, m, g,h), 4.44 (2H, d, *J* = 5.7 Hz, l), 2.67 (2H, t, *J* = 7.3 Hz, e), 2.20–2.40 (6H, m, f,i,j); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.45 (k), 142.04 (d), 138.55 (m), 131.03 (h), 129.23 (g), 128.80 (b,b'), 128.61 (o,o'), 128.38 (c,c'), 127.93 (n,n'), 127.60 (p), 125.89 (a), 43.66 (l), 36.71 (j), 35.96 (e), 34.40 (f), 28.73 (i); IR (neat) 3285 (N-H stretch), 3028, 2915, 1635 (C=O stretch), 1537 (N-H bend), 1452, 1220, 965, 740, 694 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{23}NNaO$ (M+Na): 316.1677, found 316.1681 *m/z*.

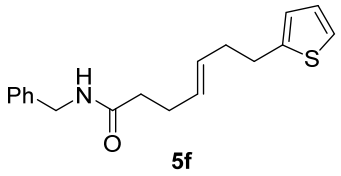


(*Z*)-**5d**

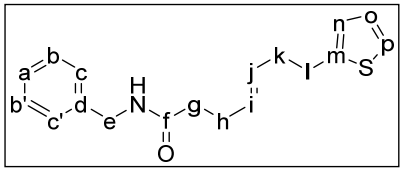
(*Z*)-7-phenyl-4-heptenecarboxylic acid benzyl amide ((*Z*)-5d). Following **GP1** with (*Z*)-**8 (**5 mmol, 1.16g), benzyl amine (2 equiv, 10 mmol, 1.1 mL) affords, after flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate), the title compound (1.08 g, 73%) as a light yellow oil; TLC analysis R_f 0.4 (60:40 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.40 (10H, m, a,b,b',c,c',n,n',o,o',p), 6.03 (1H, br s, NH), 5.45–5.55 (1H, m, h), 5.35–5.45 (1H, m, g), 4.41 (2H, d, *J* = 5.7 Hz, l), 2.69 (2H, t, *J* = 7.8 Hz, e), 2.41 (2H, q, *J* = 7.4 Hz, f), 2.33 (2H, q, *J* = 7.4 Hz, i), 2.08 (2H, t, *J* = 8.6 Hz, j); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.53 (k), 142.10 (d), 138.55 (m), 130.29 (h), 128.81 (b,b'), 128.78 (o,o'), 128.41 (g,c,c'), 127.92 (n,n'), 127.57 (p), 125.92 (a), 43.65 (l), 36.53 (j), 35.91 (e), 29.29 (f), 23.61 (i); IR (neat) 3285 (N-H stretch), 3026, 2922, 1642 (C=O stretch), 1543 (N-H bend), 1495, 1453, 728, 695 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{23}NNaO$ (M+Na): 316.1677, found 316.1681 *m/z*.



(*E*)-7-(furan-2-yl)-4-heptenecarboxylic acid benzyl amide (5e).[a] Following **GP1** with the corresponding ethyl ester ((*E*)-7-(furan-2-yl)-4-heptenecarboxylic acid ethyl ester, 5 mmol, 1.1 g) and benzyl amine (2 equiv, 10 mmol, 1.1 mL) affords, after flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate), the title compound (596 mg, 42%) as a white solid: m.p. 60.5–61.5 ºC; TLC analysis R_f 0.35 (60:40 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.40 (6H, m, a,b,b',c,c',p), 6.28 (1H, dd, *J* = 3.0 Hz, 1.9 Hz, o), 5.98 (1H, dd, *J* = 3.1 Hz, 0.6 Hz, n), 5.90 (1H, br s, NH), 5.40–5.60 (2H, m, i,j), 4.44 (2H, d, *J* = 5.7 Hz, e), 2.67 (2H, t, *J* = 7.4 Hz, l), 2.20–2.40 (6H, m, g,h,k); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.40 (f), 155.78 (m), 140.89 (p), 138.51 (d), 130.53 (i), 129.50 (j), 128.80 (b,b'), 127.92 (c,c'), 127.60 (a), 110.17 (o), 105.03 (n), 43.66 (e), 36.64 (g), 31.02 (k), 28.68 (h), 28.07 (l); IR (neat) 3293 (N-H stretch), 2916, 1632 (C=O stretch), 1538 (N-H bend), 1506, 1453, 729, 695 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{21}NNaO_2$ (M+Na): 306.1470, found 306.1477 *m/z*.



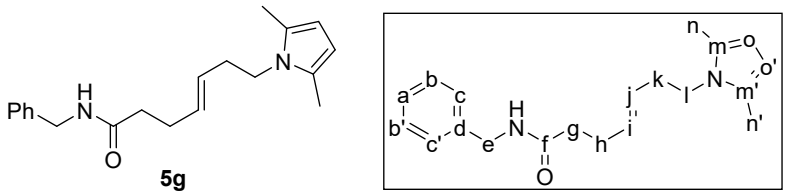
5f



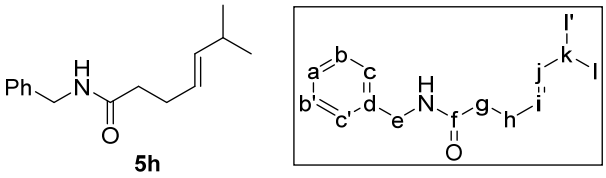
(*E*)-7-(thiophen-2-yl)-4-heptenecarboxylic acid benzyl amide (5f).[b] Following **GP1** with the corresponding ethyl ester ((*E*)-7-(thiophen-2-yl)-4-heptenecarboxylic acid ethyl ester, 5 mmol, 1.19g) and benzyl amine (2 equiv, 10 mmol, 1.1 mL) affords, after flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate), the title compound (945 mg, 63%) as a white solid: m.p. 62.0–63.0 ºC; TLC analysis R_f 0.35 (60:40 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.40 (2H, m, b,b'), 7.25–7.30 (3H, m, a, c,c'), 7.12 (1H, dd, *J* = 5.2 Hz, 0.8 Hz, p), 6.93 (1H, dd, *J* = 4.9 Hz, 3.5 Hz, o), 6.79 (1H, d, *J* = 2.6 Hz, n), 6.20 (1H, br s, NH), 5.40–5.60 (2H, m, i,j), 4.42 (2H, d, *J* = 5.7 Hz, e), 2.87 (2H, t, *J* = 7.4 Hz, l), 2.30–2.40 (4H, m, h,k), 2.26 (2H, t, *J* = 7.1 Hz, g); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.55 (f), 144.86 (m), 138.62 (d), 130.32 (i), 129.85 (j), 128.78 (b,b'), 127.89 (c,c'), 127.56 (a), 126.81 (o), 124.34 (p), 123.10 (n), 43.61 (e), 36.56 (g), 34.65 (k), 30.00 (h), 28.75 (l); IR (neat) 3291 (N-H stretch), 3030, 2915, 1629 (C=O

[a] The substrate should be used immediately after preparation or stored inside a glovebox to maintain its original quality
[b] The substrate should be used immediately after preparation or stored inside a glovebox to maintain its original quality

stretch), 1531 (N-H bend), 1453, 968, 746, 693 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{21}NNaOS$ (M+Na): 322.1242, found 322.1243 *m/z*.



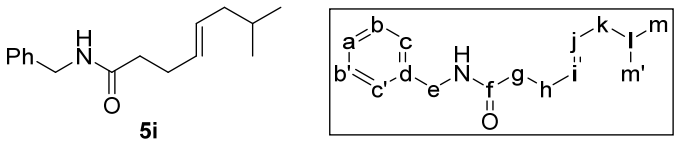
(*E*)-7-(2,5-dimethyl-1*H*-pyrrol-1-yl)-4-heptenecarboxylic acid benzyl amide (5g).[c] Following **GP1** with the corresponding ethyl ester ((*E*)-7-(2,5-dimethyl-1*H*-pyrrol-1-yl)-4-heptenecarboxylic acid ethyl ester, 5 mmol, 1.25g) and benzyl amine (2 equiv, 10 mmol, 1.1 mL) affords, after flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate), the title compound (840 mg, 54%) as a colorless oil; TLC analysis R_f 0.5 (40:60 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.40 (2H, m, b,b'), 7.25–7.35 (3H, m, a,c,c'), 5.99 (1H, br s, NH), 5.77 (2H, s, o,o'), 5.40–5.50 (2H, m, i,j), 4.44 (2H, d, *J* = 5.8 Hz, e), 3.76 (2H, t, *J* = 7.4 Hz, l), 2.35–2.45 (2H, m, h), 2.25–2.35 (2H, m, k), 2.25 (2H, t, *J* = 7.0 Hz, g, *overlapping with* n,n'), 2.23 (6H, s, n,n'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.35 (f), 138.63 (d), 131.62 (i), 128.79 (b,b',m,m'), 127.92 (c,c'), 127.58 (a), 127.40 (j), 105.12 (o,o'), 43.63 (e), 43.48 (l), 36.51 (g), 34.18 (k), 28.80 (h), 12.73 (n,n'); IR (neat) 3283 (N-H stretch), 2914, 1643 (C=O stretch), 1539 (N-H bend), 1453, 1407, 970, 743, 697 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{26}N_2NaO$ (M+Na): 333.1943, found 333.1950 *m/z*.



(*E*)-6-methyl-4-heptenecarboxylic acid benzyl amide (5h). Following **GP1** with the corresponding ethyl ester ((*E*)-6-methyl-4-heptenecarboxylic acid ethyl ester, 5 mmol, 0.85 g) and benzyl amine (2 equiv, 10 mmol, 1.1 mL) affords, after flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate), the title compound (751 mg, 65%) as a white solid: m.p. 45.0–45.5 °C; TLC analysis R_f 0.4 (60:40 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15–7.40 (5H, m, a,b,b',c,c'), 6.08 (1H, br s, NH), 5.30–5.50 (2H, m, i,j), 4.42 (2H, d, *J* = 5.7 Hz, e), 2.15–

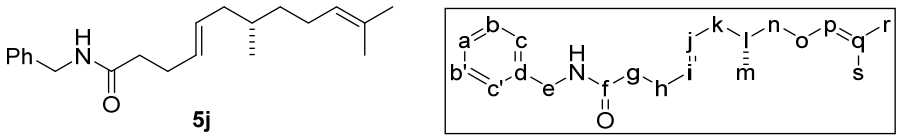
[c] The substrate should be used immediately after preparation or stored inside a glovebox to maintain its original quality

2.40 (5H, m, g,h,k), 0.95 (6H, d, J = 6.7 Hz, l,l'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.61 (f), 139.20 (d), 138.55 (j), 128.76 (b,b'), 127.88 (c,c'), 127.53 (i), 125.35 (a), 43.61 (e), 36.73 (g), 31.04 (k), 28.69 (h), 22.60 (l,l'); IR (neat) 3292 (N-H stretch), 2959, 2928, 2870, 1633 (C=O stretch), 1534 (N-H bend), 1454, 1407, 968, 746, 694 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{21}NNaO$ (M+Na): 254.1521, found 254.1526 *m/z*.



5i

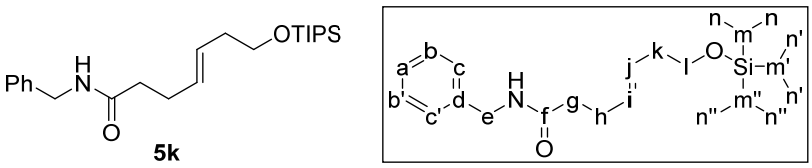
(*E*)-7-methyl-4-octenecarboxylic acid benzyl amide (5i). Following **GP1** with the corresponding ethyl ester ((*E*)-7-methyl-4-octenecarboxylic acid ethyl ester, 5 mmol, 0.92 g) and benzyl amine (2 equiv, 10 mmol, 1.1 mL) affords, after flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate), the title compound (873 mg, 71%) as a white semi-solid; TLC analysis R_f 0.4 (60:40 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.40 (2H, m, b,b'), 7.20–7.30 (3H, m, a,c,c'), 6.09 (1H, br s, NH), 5.35–5.55 (2H, m, i,j), 4.42 (2H, d, J = 5.6 Hz, e), 2.30–2.40 (2H, m, h), 2.25–2.30 (2H, m, g) 1.87 (2H, t, J = 6.6 Hz, k), 1.50–1.65 (1H, m, l), 0.87 (6H, d, J = 6.6 Hz, m,m') ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.57 (f), 138.55 (d), 130.78 (i), 129.52 (j), 128.76 (b,b'), 127.89 (c,c'), 127.53 (a), 43.63 (e), 42.00 (k), 36.75 (g), 28.79 (h), 28.45 (l), 22.37 (m,m'); IR (neat) 3286 (N-H stretch), 2953, 2923, 2868, 1642 (C=O stretch), 1544 (N-H bend), 1454, 967, 696 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{23}NNaO$ (M+Na): 268.1677, found 268.1689 *m/z*.



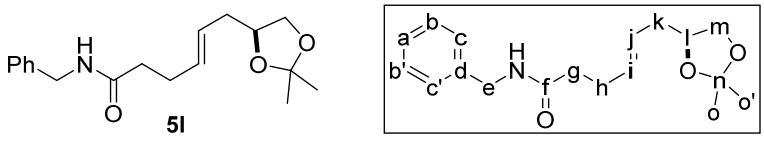
5j

(*S*,*E*)-7,11-dimethyl-4,10-dodecadienecarboxylic acid benzyl amide (5j). Following **GP1** with the corresponding ethyl ester ((*S*,*E*)-7,11-dimethyl-4,10-dodecadienecarboxylic acid ethyl ester, 5 mmol, 1.26 g) and benzyl amine (2 equiv, 10 mmol, 1.1 mL) affords, after flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate), the title compound (1.14 g, 73%) as a colorless oil; TLC analysis R_f 0.4 (60:40 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = +6.2° (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.35 (2H, m, b,b'), 7.25–7.30 (3H, m, a,c,c'), 6.22

(1H, br s, NH), 5.35–5.50 (2H, m, i,j), 5.11 (1H, tt, J = 7.2 Hz, 1.3 Hz, p), 4.40 (2H, d, J = 5.8 Hz, e), 2.30–2.40 (2H, m, h), 2.25–2.30 (2H, m, g), 1.90–2.05 (3H, m, k,o), 1.75–1.85 (1H, m, k), 1.70 (3H, s, r), 1.62 (3H, s, s),1.40–1.50 (1H, m, l), 1.25–1.40 (1H, m, n), 1.10–1.20 (1H, m, n), 0.86 (3H, d, J = 6.6 Hz, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.62 (f), 138.58 (d), 131.17 (q), 130.47 (i), 129.69 (j), 128.73 (b,b'), 127.86 (c,c'), 127.49 (a), 124.98 (p), 43.60 (e), 40.05 (k), 36.77 (n), 36.71 (g), 32.77 (l), 28.83 (h), 25.85 (r), 25.70 (o), 19.46 (m), 17.77 (s); IR (neat) 3277 (N-H stretch), 2959, 2911, 1643 (C=O stretch), 1545 (N-H bend), 1453, 968, 696 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{31}NNaO$ (M+Na): 336.2303, found 336.2316 *m/z*.

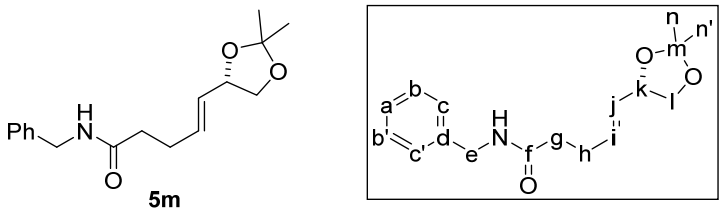


(*E*)-7-((triisopropylsilyl)oxy)-4-heptenecarboxylic acid benzyl amide (5k). Following **GP1** with the corresponding ethyl ester ((*E*)-7-((triisopropylsilyl)oxy)-4-heptenecarboxylic acid ethyl ester, 5 mmol, 1.64 g) and benzyl amine (2 equiv, 10 mmol, 1.1 mL) affords, after flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate), the title compound (1.46 g, 75%) as a colorless oil; TLC analysis R_f 0.5 (60:40 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.40 (5H, m, a,b,b',c,c'), 6.14 (1H, br s, NH), 5.40–5.55 (2H, m, i,j), 4.41 (2H, d, J = 5.7 Hz, e), 3.67 (2H, t, J = 6.8 Hz, l), 2.20–2.40 (6H, m, g,h,k), 1.00–1.15 (21H, m, m,m',m'',n,n',n''); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.55 (f), 138.55 (d), 130.49 (i), 128.75 (b,b'), 128.29 (j), 127.84 (c,c'), 127.51 (a), 63.44 (l), 43.61 (e), 36.52 (k), 36.50 (g), 28.85 (h), 18.14 (n,n',n''), 12.11 (m,m',m''); IR (neat) 3283 (N-H stretch), 2942, 2864, 1644 (C=O stretch), 1545 (N-H bend), 1455, 1100, 881, 679 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{39}NNaO_2Si$ (M+Na): 412.2648, found 412.2652 *m/z*.

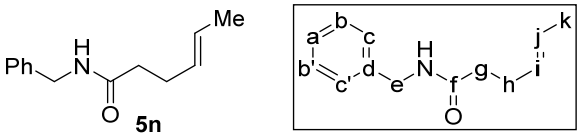


(*S,E*)-6-(2,2-dimethyl-1,3-dioxolan-4-yl)-4-hexenecarboxylic acid benzyl amide (5l). Following **GP1** with the corresponding ethyl ester ((*S,E*)-6-(2,2-dimethyl-1,3-dioxolan-4-yl)-4-hexenecarboxylic acid ethyl ester, 5 mmol, 1.2 g) and benzyl amine (2 equiv, 10 mmol, 1.1 mL)

affords, after flash chromatography on silica gel (60:40-30:70 hexanes:ethyl acetate), the title compound (1.05 g, 69%) as a white semi-solid; TLC analysis R_f 0.25 (60:40 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = +19.2° (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.35 (2H, m, b,b'), 7.20–7.30 (3H, m, a,c,c'), 6.11 (1H, br s, NH), 5.40–5.60 (2H, m, i,j), 4.40 (2H, d, *J* = 5.7 Hz, e), 4.00–4.10 (1H, m, l), 3.97 (1H, dd, *J* = 8.0 Hz, 6.0 Hz, m), 3.52 (1H, dd, *J* = 7.9 Hz, 7.0 Hz, m), 2.30–2.40 (3H, m, h,k), 2.25–2.30 (2H, m, g), 2.15–2.25 (1H, m, k), 1.40 (3H, s, o), 1.33 (3H, s, o'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.32 (f), 138.53 (d), 131.82 (i), 128.76 (b,b'), 127.86 (c,c'), 127.54 (a), 126.52 (j), 109.00 (n), 75.53 (l), 68.92 (m), 43.60 (e), 36.92 (k), 36.37 (g), 28.70 (h), 27.01 and 25.74 (o,o'); IR (neat) 3291 (N-H stretch), 2984, 2933, 1643 (C=O stretch), 1541 (N-H bend), 1454, 1369, 1213, 1154, 1058, 969, 697 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{25}NNaO_3$ (M+Na): 236.1732, found 326.1739 *m/z*.

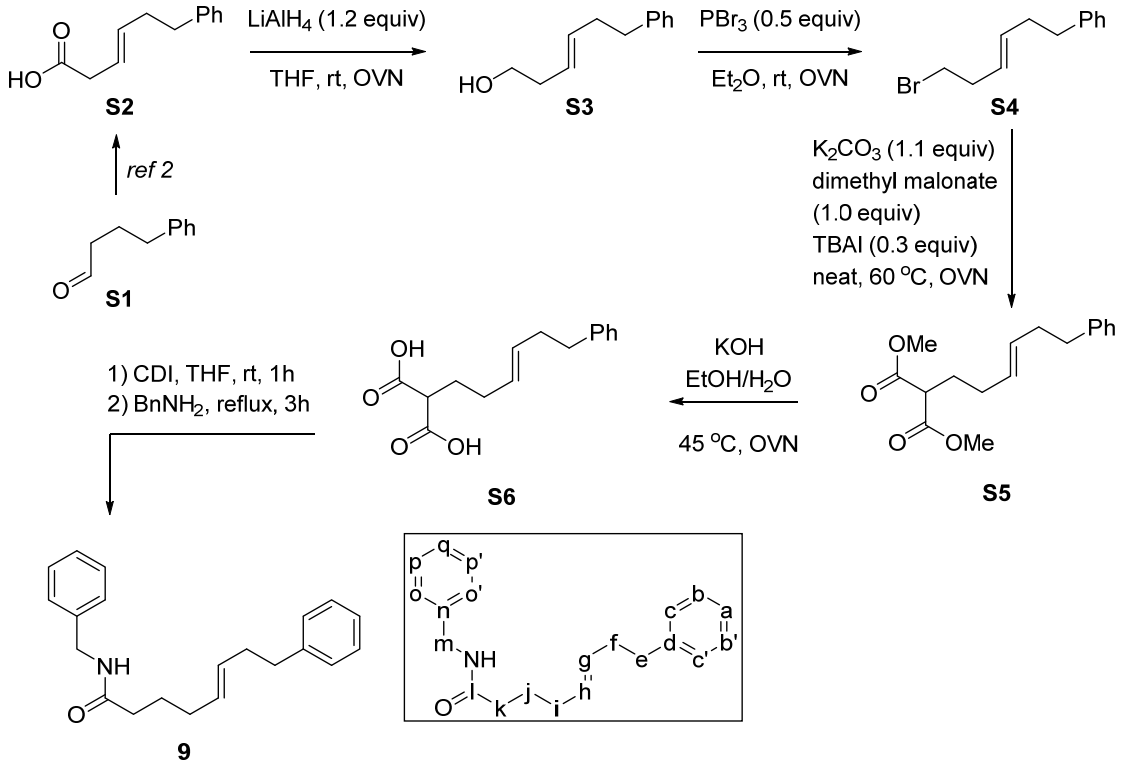


(*S,E*)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-4-pentenecarboxylic acid benzyl amide (5m). Following **GP1** with the corresponding ethyl ester ((*S,E*)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-4-pentenecarboxylic acid ethyl ester, 5 mmol, 1.14 g) and benzyl amine (2 equiv, 10 mmol, 1.1 mL) affords, after flash chromatography on silica gel (60:40-30:70 hexanes:ethyl acetate), the title compound (913 mg, 63%) as a colorless oil; TLC analysis R_f 0.25 (60:40 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = +25.1° (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.35 (2H, m, b,b'), 7.25–7.30 (3H, m, a,c,c'), 6.02 (1H, br s, NH), 5.79 (1H, td, *J* = 15.3 Hz, 6.5 Hz, i), 5.49 (1H, dd, *J* = 15.4 Hz, 7.7 Hz, j), 4.35–4.50 (1H, m, k), 4.41 (2H, d, *J* = 5.7 Hz, e), 4.03 (1H, dd, *J* = 8.1 Hz, 6.1 Hz, l), 3.52 (1H, dd, *J* = 8.0 Hz, 8.0 Hz, l), 2.35–2.45 (2H, m, h), 2.25–2.35 (2H, m, g), 1.41 (3H, s, n), 1.38 (3H, s, n'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.96 (f), 138.41 (d), 133.72 (i), 128.80 (b,b'), 128.77 (j), 127.91 (c,c'), 127.62 (a), 109.25 (m), 69.48 (k), 43.68 (e), 35.84 (g), 28.23 (h), 26.83 and 26.01 (n,n'); IR (neat) 3294 (N-H stretch), 2985, 2933, 2872, 1644 (C=O stretch), 1541 (N-H bend), 1454, 1369, 1244, 1213, 1155, 1057, 1028, 967, 859, 732, 697 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{23}NNaO_3$ (M+Na): 312.1576, found 312.1581 *m/z*.



(*E*)-4-hexenecarboxylic acid benzyl amide (5n). Following **GP1** with the corresponding ethyl ester ((*E*)-4-hexenecarboxylic acid ethyl ester, 5 mmol, 712 mg) and benzyl amine (2 equiv, 10 mmol, 1.1 mL) affords, after flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate), the title compound (691 mg, 68%) as a white solid: m.p 58.5–59.5 °C; TLC analysis R_f 0.4 (60:40 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.35 (2H, m, b,b'), 7.20–7.30 (3H, m, a,c,c'), 6.20 (1H, br s, NH), 5.25–5.55 (2H, m, i,j), 2.30–2.35 (2H, m, h), 2.20–2.30 (2H, m, g), 1.64 (3H, d, J = 5.8 Hz, k); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.64 (f), 138.59 (d), 129.64 (i), 128.74 (b,b'), 127.85 (c,c'), 127.49 (a), 126.43 (j), 43.58 (e), 36.60 (g), 28.75 (h), 18.00 (k); IR (neat) 3289 (N-H stretch), 2918, 1633 (C=O stretch), 1548 (N-H bend), 1493, 1452, 1234, 964, 747, 697 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_{17}NNaO$ (M+Na): 226.1208, found 226.1208 *m/z*.

Preparation sequence of γ,δ-unsaturated benzyl amide 9



To a cooled (0 ºC) solution of (*E*)-6-phenylhex-3-enoic acid[2] **S2** (13.3 mmol, 2.53 g) in THF (50 mL) was added lithium aluminum hydride (LAH, 1.05 equiv, 14.0 mmol, 530 mg). The resulting mixture was warmed to room temperature and stirred overnight. The reaction mixture was quenched with 5N KOH (1 mL) and water (0.5 mL). Following by 30-min stir, the resultant mixture was filtered through a pad of celite and wash with ethyl acetate (2 x 5 mL). The filtrate was dried (anhyd. Na_2SO_4) and concentrated under reduced pressure to give the crude yellow oil **S3** in quantitative yield which was used in the next step without further purification.

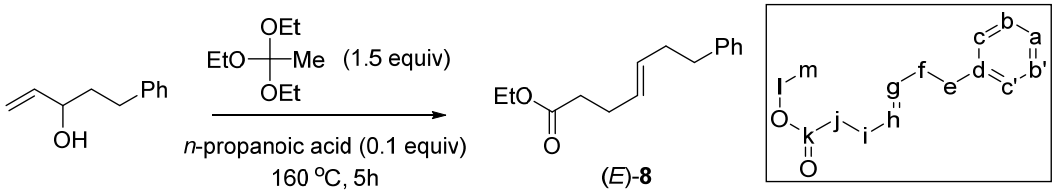
To a cooled (0 ºC) solution of (*E*)-6-phenylhex-3-en-1-ol **S3** (13.1 mmol, 2.31 g) in diethyl ether (20 mL) was added PBr_3 (0.5 equiv, 6.6 mmol, 0.62 mL) dropwise. The resultant mixture was slowly warmed to room temperature and stirred overnight. The reaction mixture was quenched with brine solution (20 mL). The organic layer was separated and the aqueous layer was washed with ethyl acetate (2 x 20 mL). The combined organic extracts were concentrated under reduced pressure, passed through a short pad of silica gel eluting with 20% ethyl acetate:hexanes (50 mL), and concentrated again under reduced pressure to afford the crude yellow oil **S4** in 92% yield which was used in the next step without further purification.

A neat mixture of (*E*)-(6-bromohex-3-en-1-yl)benzene **S4** (6 mmol, 1.43 g), dimethyl malonate (6 mmol, 1.0 equiv, 0.69 mL), K_2CO_3 (6.6 mmol, 1.1 equiv, 910 mg) and TBAI (1.8 mmol, 0.3 equiv, 665 mg) was stirred vigorously at 60 ºC for 24 hrs. The resultant mixture was cooled down to room temperature, diluted with ethyl acetate, filtered, washed with ethyl acetate (3 x 5 mL), and concentrated under reduced pressure to give the crude yellow oil **S5** in 81% yield which was used in the next step without further purification.

To a solution of dimethyl (*E*)-2-(6-phenylhex-3-en-1-yl)malonate **S5** (2.2 mmol, 635 mg) in EtOH:water (5 mL, 4:1) was added KOH (7.2 mmol, 3.2 equiv, 405 mg). The resultant mixture was heated to 45 ºC. After a 16h stir, the mixture was cooled to room temperature, concentrated under reduced pressure and poured into a solution of diethyl ether:hexanes (5 mL, 1:4) and water (5 mL). The resulting mixture was acidified with conc. H_2SO_4 (0.4 mL) and adjusted to pH = 1 by dilute HCl (3M). After extraction with EtOAc (3 x 10 mL), the organic layers were combined, dried (anhyd. Na_2SO_4) and concentrated under reduced pressure to give the crude off-white solid **S6** in 96% yield which was used in the next step without further purification.

To a solution of (*E*)-2-(6-phenylhex-3-en-1-yl)malonic acid **S6** (2.1 mmol, 550 mg) in THF (5 mL) was added CDI (2.3 mmol, 1.1 equiv, 372 mg) portion wise under positive nitrogen.[3] The resulting mixture was stirred at room temp for 2h, then benzyl amine (3.2 mmol, 1.5 equiv, 0.35 mL) was added in one portion. The resultant mixture was refluxed for 3h, cooled to room temp, and concentrated under reduced pressure. The obtained residue was then dissolved in 10 mL EtOAc and washed with a 10 mL aqueous solution of citric acid monohydrate (2.1 mmol, 1 equiv, 441 mg) and a saturated sodium bicarbonate (10 mL). The organic extract was dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate) affords the title compound **9** (473 mg, 73%) as a white solid: m.p. 67.0–68.0 ºC; TLC analysis R_f 0.4 (60:40 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.40 (7H, m, b,b',o,o',p,p',q), 7.15–7.25 (3H, m, a,c,c'), 5.68 (1H, br s, NH), 5.30–5.50 (2H, m, g,h), 4.44 (2H, d, *J* = 5.7 Hz, m), 2.69 (2H, t, *J* = 7.4 Hz, e), 2.34 (2H, q, *J* = 6.6 Hz, f), 2.11 (2H, t, *J* = 7.4 Hz, k), 2.04 (2H, q, *J* = 6.6 Hz, i), 1.65–1.80 (2H, m, j); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.92 (l), 142.08 (d), 138.54 (n), 130.66 (g), 130.17 (h), 128.83 (b,b'), 128.64 (p,p'), 128.37 (c,c'), 128.00 (o,o'), 127.64 (q), 125.84 (a), 43.70 (m), 36.95 (e), 35.80 (k), 34.19 (f), 31.95 (i), 25.37 (j); IR (neat) 3290 (N-H stretch), 2924, 2848, 1629 (C=O stretch), 1550 (N-H bend), 1494, 1452, 726, 693 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{25}NNaO$ (M+Na): 330.1834, found 330.1833 *m/z*.

General procedure for the preparation of (*E*)-γ,δ-unsaturated ethyl esters via Claisen-Johnson rearrangement (GP2)[4]

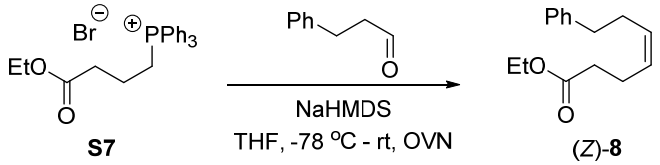


(*E*)-7-phenyl-4-heptenecarboxylic acid ethyl ester ((*E*)-8).[4] A mixture of 5-phenylpent-1-en-3-ol (61.6 mmol, 10.1 g), triethyl orthoacetate (93.3 mmol, 1.5 equiv, 17.1 mL), and *n*-propanoic acid (6.6 mmol, 0.11 equiv, 0.5 mL) was heated with Dean-Stark apparatus at 160 ºC for 5h. After cooling to room temperature, the reaction mixture was quenched with satd. $NaHCO_3$ (10 mL), then dilute with DCM (100 mL) and HCl (1M, 100 mL). After a 2h stir, the organic layer was separated, and the aqueous layer was washed with DCM (2 x 50 mL). The organic layers were

combined, dried (anhyd. Na_2SO_4) and concentrated under reduced pressure affords, after flash chromatography on silica gel (95:5 hexanes:ethyl acetate), the title compound (11.9 g, 83%) as a yellow liquid; TLC analysis R_f 0.4 (90:10 hexanes:ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.35 (2H, m, b,b'), 7.30–7.35 (3H, m, a,c,c'), 5.45–5.60 (2H, m, g,h), 4.18 (2H, q, *J* = 7.1 Hz,, l), 2.72 (2H, t, *J* = 7.3 Hz, e), 2.30–2.40 (6H, m, f,i,j), 1.30 (3H, t, *J* = 7.1 Hz, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.27 (k), 142.07 (d), 130.85 (h), 128.96 (g), 128.59 (b,b'), 128.39 (c,c'), 125.90 (a), 60.35 (l), 36.09 (e), 34.49 (j), 34.44 (f), 28.04 (i), 14.42 (m); IR (neat) 2980, 2925, 1732 (C=O stretch), 1453, 1371, 1247, 1175, 1032, 968, 745, 698 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{20}NaO_2$ (M+Na): 255.1361, found 255.1364 *m/z*.

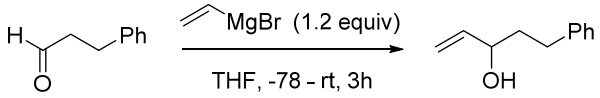
The above ester (*E*)-**8** was isolated via column chromatography for screening purpose. All other (*E*)-esters were pass through a short pad of silica gel eluting with 10% EtOAc:hexanes, concentrated under reduced pressure, and used without further purification. *Note:* the reaction was typically done under air. For furan-, thiophene-, and pyrrole-containing compounds, it should be done under nitrogen to prevent partial decomposition of the products.

Preparation of (*Z*)-7-phenyl-4-heptenecarboxylic acid ethyl ester ((*Z*)-8) via Wittig reaction



The Wittig reagent **S7** was prepared from 4-bromobutyricacid ethyl ester and triphenylphosphine as previously reported in literature.[5] To a cooled (0 °C) solution of **S7** (11 mmol, 5 g) in THF (40 mL) was added NaHMDS (1.1 equiv, 1M, 12 mmol, 12 mL) dropwise. The resultant mixture was stirred at 0 °C in 30 mins. After cooling down to -78 °C, 3-phenylpropanal (1.1 equiv, 12 mmol, 1.6 mL) was added dropwise. The resultant mixture was slowly warmed to room temp and stirred overnight. The reaction was quenched with satd. ammonium chloride (20 mL) and extracted with EtOAc (3 x 30 mL). The organic layers were combined, washed with brine, dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. The obtained residue was dilute with minimum amount of DCM, passed through a short pad of silica gel eluting with 10% EtOAc:hexanes, concentrated under reduced pressure to give a crude (*Z*)-**8** as a yellow liquid (1.3 g, 51%), which was used in the next step without further purification.

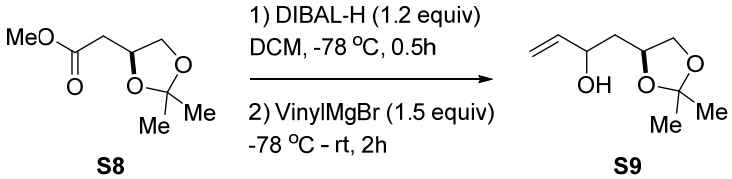
General procedure for the preparation of allylic alcohol with aldehyde and vinyl magnesium bromide (GP3)[4]



To a cooled (-78 ºC) solution of vinyl magnesium bromide (140 mmol, 1.2 equiv, 1M, 140 mL) was added 3-phenylpropanal (120 mmol, 16 mL) dropwise. The resultant mixture was slowly warmed to room temp and stirred for a total of 3h. After quenching with satd. ammonium chloride, it was continued stirring for 15 more mins. The pH was adjusted to 3-4 using dilute HCl (1M). After extraction with EtOAc (3 x 100 mL), the organic layers were combined, washed with brine, dried (anhyd. Na_2SO_4) and concentrated under reduced pressure to give the crude yellow liquid (18.2 g, 93%) which was used in the next step without further purification.

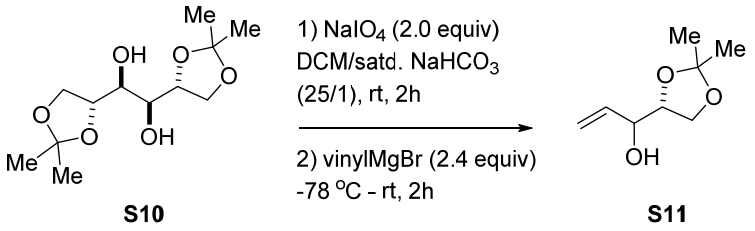
The above procedure was applied for all allylic alcohols, except for the two dioxolane-containing compounds.

Preparations of dioxolane-containing allylic alcohols



1-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)but-3-en-2-ol (S9). The preparation of (4*S*)-(2,2-dimethyl-[1,3]-dipxolan-4-yl) acetic acid methyl ester **S8** from (L)-malic acid was previously reported in literature.[6] To the solution of ester **S8** (20 mmol, 3.5 g) in DCM (80 mL) was slowly added DIBAL-H (1M, 1.2 equiv, 24 mmol, 24 mL) at -78 ºC. The resulting mixture was stirred at -78 ºC for 30 mins, then vinyl magnesium bromide (1M, 1.5 equiv, 30 mmol, 30 mL) was slowly added at the same temperature. The resultant mixture was stirred at -78 ºC for 30 mins and allowed to warm to room temperature and stirred for another 1.5h. The reaction mixture was carefully quenched with NaOH (1M, 15 mL). After filtering through a pad of celite, a filtrate was washed with water and brine. The organic layer was dried (anhyd. Na_2SO_4) and carefully concentrated

under reduced pressure to give the crude yellow liquid (3.06 g, 89%) which was used in the next step without further purification.

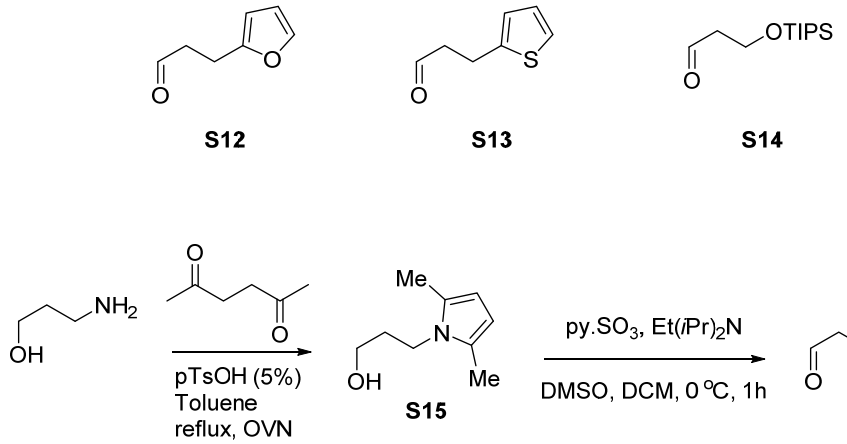


S10 **S11**

1-((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)prop-2-en-1-ol (S11). The preparation of (1*S*,2*S*)-1,2-bis((*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)ethane-1,2-diol **S10** from (D)-mannitol was previously reported in literature.[7] To a solution of **S10** (21.7 mmol, 5.7 g) in DCM (65 mL) was added satd. $NaHCO_3$ (2.6 mL). While the resulting mixture is vigorously stirred, $NaIO_4$ (2 equiv, 43.4 mmol, 9.3 g) was added portion wise. After stirring at room temp for 4h, the suspension was filtered through a pad of celite, flushed with nitrogen, and used in the next step without further purification.

To the above solution, vinyl magnesium bromide (2.4 equiv with respect to **S10**, 1M, 52 mmol, 52 mL) was added slowly at -78 ºC. The resultant mixture was stirred at -78 ºC for 30 mins and allowed to warm to room temperature and stirred for another 1.5h. The reaction mixture was carefully quenched with NaOH (1M, 35 mL). After filtering through a pad of celite, a filtrate was washed with water and brine. The organic layer was dried (anhyd. Na_2SO_4) and carefully concentrated under reduced pressure to give the crude yellow liquid (4.46 g, 65%) which was used in the next step without further purification.

Preparations of aldehydes S12–14 and S16



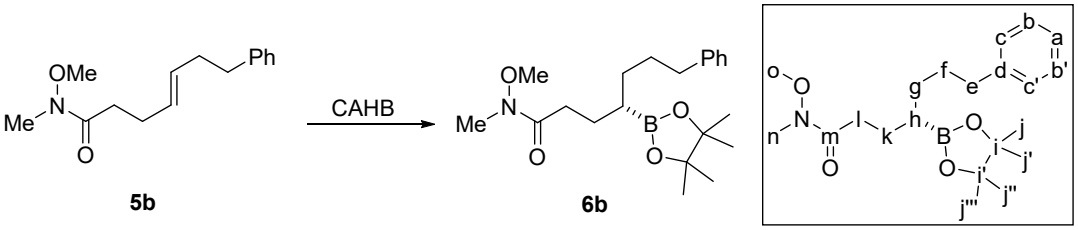
S12,[8] **S13,**[9] and **S14**[10] were prepared as described in literature.

3-(2,5-dimethyl-1*H*-pyrrol-1-yl)propanal (S16). The solution of 3-aminopropanol (59.7 mmol, 4.56 mL), 2,5-hexanedione (59.7 mmol, 7.0 mL), and *p*-toluenesulfonic acid monohydrate (0.05 equiv, 3 mmol, 570 mg) in toluene (50 mL) was reflux with Dean-Stark apparatus overnight. The resultant mixture was cooled to room temp and washed with water. The organic layer was separated and the aqueous layer was extracted with DCM (3 x 20 mL). The organic layers were combined, dried (anhyd. Na_2SO_4) and concentrated under reduced pressure to give crude **S15** as a brown liquid in (9.1 g, quantitative) which was used in the next step without further purification.

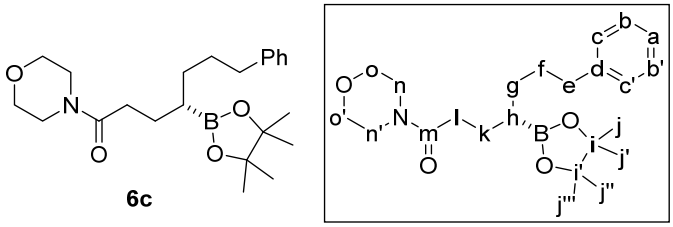
To a cooled (0 °C) solution of crude **S15** (13.7 mmol, 2.1 g) in DCM (40 mL) was added DMSO (6 equiv, 82.1 mmol, 5.8 mL), Et(*i*Pr)$_2$N (3 equiv, 41 mmol, 7.1 mL) and sulfur trioxide pyridine complex (2 equiv, 27.4, 4.35 g) sequentially. The resultant mixture was stirred at 0 °C for 1h before quenching with brine (20 mL). The aqueous layer was washed with Et_2O (3 x 20 mL), and the combined organic layers were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure to give crude **S16** as a brown liquid (1.61 g, 78%) which was used in the next step without further purification.

General procedure for CAHB of *γ,δ*-unsaturated amides without subsequent oxidation. (GP4)

*Note: **6c** and **6d** were obtained in a gram scale without loss in selectivity.*

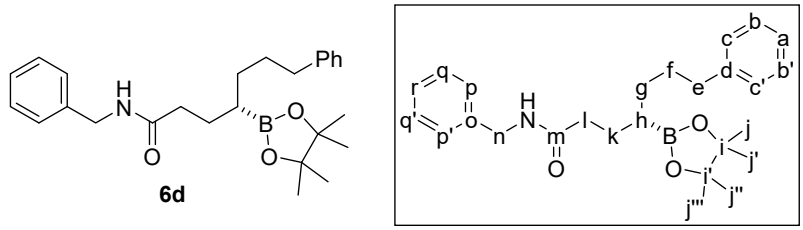


(*S*)-7-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanecarboxylic acid Weinreb amide (6b). To a yellow solution of 2 mol% [$Rh(nbd)_2BF_4$/ 2(*R*)-**L1**] (i.e., $Rh(nbd)_2BF_4$ (3.9 mg, 0.01 mmol) and (*R*)-(BINOL)PN(Me)Ph **L1** (8.9 mg, 0.021 mmol)) in THF (2.0 mL) was added γ,δ-unsaturated amide **5b** (130 mg, 0.528 mmol) as a solution in THF (2.0 mL). To the resulting solution was added dropwise a solution of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinBH, **B1**, 102 mg, 0.8 mmol) in THF (1.0 mL). The mixture was then stirred at 40 ºC for 12h. Afterwards, the reaction was concentrated under reduced pressure and purified via flash chromatography on silica gel (90:10-50:50 hexanes:ethyl acetate) to afford the title compound (136 mg, 69%) as a yellow oil: TLC analysis R_f 0.4 (60:40 hexanes:ethyl acetate); $[\alpha]_D^{20} = +5.1^o$ (*c* 2.0, $CHCl_3$); ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.87; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.30 (2H, m, b,b'), 7.15–7.25 (3H, m, a,c,c'), 3.67 (3H, s, o), 3.18 (3H, s, n), 2.62 (2H, d, *J* = 7.6 Hz, e), 2.30–2.60 (2H, m, l), 1.40–1.80 (6H, m, f,g,k), 1.26 (12H, s, j,j',j'',j'''), 1.00–1.15 (1H, m, h); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.93 (m), 142.89 (d), 128.50 (b,b'), 128.31 (c,c'), 125.63 (a), 83.09 (i,i'), 61.29 (o), 36.30 (e), 32.28 (n), 31.71 (l), 31.01 (f), 31.00 (g), 26.30 (k), 24.97 and 24.93 (j,j',j'',j'''); IR (neat) 2976, 2930, 2857, 1663 (C=O stretch), 1380 (C-N stretch), 1314, 1142, 699 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{34}BNNaO_4$ (M+Na): 398.2479, found 398.2496 *m/z*.



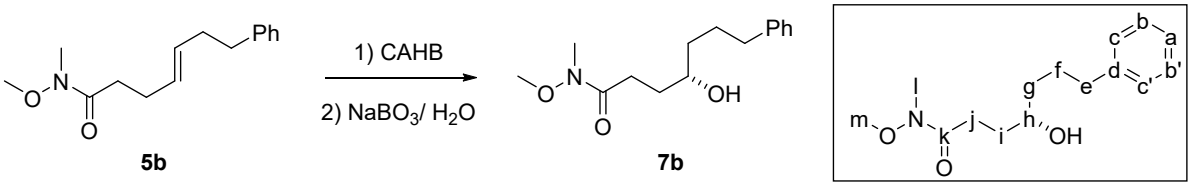
(*S*)-7-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanecarboxylic acid morpholino amide (6c). Following **GP4** with **5c** (1.01 g, 3.7 mmol) affords, after flash chromatography on silica gel (90:10-40:60 hexanes:ethyl acetate), the title compound (1.22 g,

82%) as a yellow oil: TLC analysis R_f 0.4 (40:60 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = +0.3° (*c* 2.0, $CHCl_3$); ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.34; ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.35 (2H, m, b,b'), 7.10–7.25 (3H, m, a,c,c'), 3.55–3.70 (6H, m, n,n',o,o'), 3.40–3.50 (2H, m, n,n'), 2.61 (2H, d, *J* = 7.2 Hz, e), 2.25–2.40 (2H, m, l), 1.40–1.80 (6H, m, f,g,k), 1.24 (12H, s, j,j',j'',j'''), 1.00–1.10 (1H, m, h); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.11 (m), 144.78 (d), 128.49 (b,b'), 128.32 (c,c'), 125.67 (a), 83.17 (i,i'), 67.06 and 66.86 (o,o'), 46.19 and 41.95 (n.n'), 36.25 (e), 33.08 (l), 30.92 (f), 30.89 (g), 26.99 (k), 25.00 and 24.94 (j,j',j'',j'''); IR (neat) 2974, 2924, 2854, 1644 (C=O stretch), 1425, 1380 (C-N stretch), 1142, 1114, 699 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{36}BNNaO_4$ (M+Na): 424.2635, found 424.2648 *m/z*.

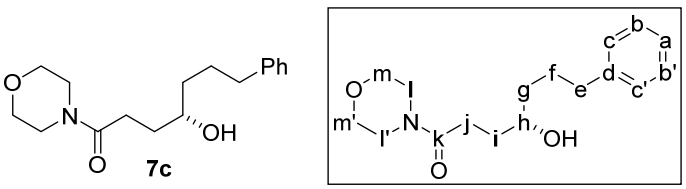


(*S*)-7-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptanecarboxylic acid benzyl amide (6d). Following **GP4** with 0.5 mol% $[Rh(nbd)_2BF_4$/ 2(*R*)-**L1**] and **5d** (1.08 g, 3.7 mmol) affords, after flash chromatography on silica gel (90:10-40:60 hexanes:ethyl acetate), the title compound (1.26 g, 81%) as a yellow oil: TLC analysis R_f 0.3 (60:40 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = +2.4° (*c* 2.0, $CHCl_3$); ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.51; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30–7.40 (2H, m, q,q'), 7.25–7.30 (5H, m, b,b',c,c',r), 7.15–7.25 (3H, m, a,p,p'), 6.00 (1H, br s, NH), 4.44 (2H, d, *J* = 5.8 Hz, n), 2.61 (2H, t, *J* = 7.6 Hz, e), 2.15–2.30 (2H, m, l), 1.70–1.85 (2H, m, k), 1.60–1.70 (2H, m, f), 1.50–1.60 (1H, m, g), 1.40–1.50 (1H, m, g), 1.23 (12H, s, j,j',j'',j'''), 1.00–1.10 (1H, m, h); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.19 (m), 142.82 (d), 138.60 (o), 128.78 (q,q'), 128.51 (b,b'), 128.34 (c,c'), 128.00 (p,p'), 127.55 (r), 125.69 (a), 83.25 (i,i'), 43.72 (n), 36.50 (l), 36.26 (e), 30.98 (f), 30.94 (g), 27.49 (k), 24.95 (j,j',j'',j'''); IR (neat) 3285 (N-H stretch), 2976, 2926, 2856, 1644 (C=O stretch), 1541 (N-H bend), 1454, 1379 (C-N stretch), 1315, 1141, 747, 697 cm^{-1}; HRMS (ESI) calcd. for $C_{26}H_{36}BNNaO_3$ (M+Na): 444.2686, found 444.2701 *m/z*.

General procedure for CAHB-oxidation sequence with $NaBO_3$/ H_2O (GP5).



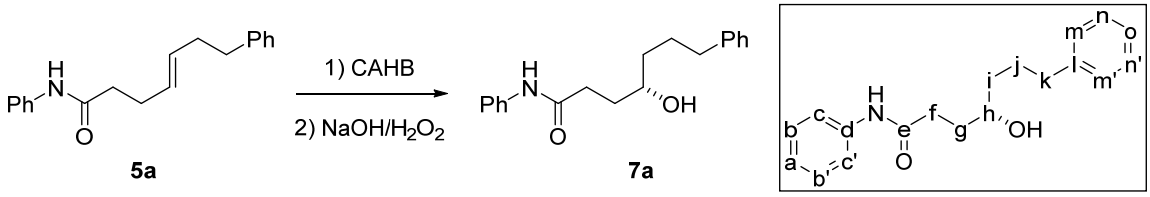
(*S*)-4-hydroxy-7-phenyl-heptanecarboxylic acid Weinreb amide (7b). Following **GP4** with **5b** (130 mg, 0.528 mmol) without purification, the obtained residue was taken up in THF (1.5 mL and water (1.5 mL). $NaBO_3$-tetrahydrate (231 mg, 1.5 mmol) was added to the resultant mixture. After a 5h vigorous stir, the reaction was dilute with water (3 mL) and EtOAc (5 mL). The organic layer was separated and the aqueous layer was extract with EtOAc (2 x 3 mL). The combined organic layers were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure affords, after flash chromatography on silica gel (80:20-20:80 hexanes:ethyl acetate), the title compound (95 mg, 68%) as a colorless oil; TLC analysis R_f 0.5 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20} = -12.5^o$ (*c* 2.0, $CHCl_3$); er of **7b** was determined by using harsh oxidation ($NaOH/H_2O_2$) instead of $NaBO_3$-tetrahydrate to form lactone **23** followed by $Al(Me)_3$-assisted transamidation with benzyl amine to generate **7d** (procedures described *vide infra*): Chiral HPLC analysis (Chiralpak-IC, 60:40 hexanes:isopropanol, flow rate = 1.3 mL/min) showed peaks at 26 minutes (4.0% (*R*)) and 30 minutes (96.0% (*S*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.30 (2H, m, b,b'), 7.15–7.25 (3H, m, a,c,c'), 3.70 (3H, s, m), 3.60–3.70 (1H, m, h, *overlapping with* m), 3.20 (3H, s, l), 2.74 (1H, br s, OH), 2.66 (2H, t, *J* = 7.6 Hz, e), 2.50–2.70 (2H, m, j, *overlapping with* e), 1.80–1.90 (2H, m, f,i), 1.65–1.75 (2H, m, f,i), 1.45–1.65 (2H, m, g); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.19 (k), 142.55 (d), 128.54 (b,b'), 128.38 (c,c'), 125.78 (a), 71.45 (h), 61.35 (m), 37.36 (g), 35.99 (e), 32.37 (l), 31.74 (i), 28.63 (j), 27.62 (f); IR (neat) 3430 (O-H stretch), 2933, 2858, 1639 (C=O stretch), 1452, 1416, 1386, 1177, 994, 748, 699 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{23}NNaO_3$ (M+Na): 288.1576, found 288.1583 *m/z*.



(*S*)-4-hydroxy-7-phenyl-heptanecarboxylic acid morpholino amide (7c). Following **GP5** with **5c** (144 mg, 0.528 mmol) affords, after flash chromatography on silica gel (80:20-70:30

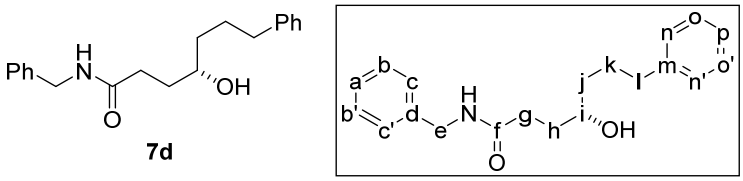
hexanes:ethyl acetate, then switch to 50:50-20:80 hexanes:acetone), the title compound (125 mg, 81%) as a colorless oil; TLC analysis R_f 0.7 (20:80 hexanes:acetone); $[\alpha]_D^{20} = -5.1^o$ (*c* 2.0, $CHCl_3$); er of **7c** was determined by boric acid-catalyzed transamidation with benzyl amine to form **7d**:[11] Chiral HPLC analysis (Chiralpak-IC, 60:40 hexanes:isopropanol, flow rate = 1.3 mL/min) showed peaks at 28 minutes (5.5 0% (*R*)) and 31 minutes (94.5% (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.30 (2H, m, b,b'), 7.15–7.20 (3H, m, a,c,c'), 3.55–3.70 (7H, m, h,l,l',m,m'), 3.40–3.50 (2H, m, l,l'), 2.64 (2H, t, *J* = 7.6 Hz, e), 2.46 (2H, t, *J* = 7.0 Hz, j), 1.75–1.90 (2H, m, f,i), 1.60–1.75 (2H, m, f,i), 1.45–1.60 (2H, m, g); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.44 (k), 142.50 (d), 128.53 (b,b'), 128.39 (c,c'), 125.83 (a), 71.28 (h), 66.95 and 66.68 (m,m'), 46.11 and 42.14 (l,l'), 37.44 (g), 35.97 (e), 32.11 (i), 29.75 (j), 27.62 (f); IR (neat) 3418 (O-H stretch), 2919, 2855, 1622 (C=O stretch), 1432, 1271, 1232, 1114, 1068, 1031, 748, 699 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{25}NNaO_3$ (M+Na): 314.1732, found 314.1743 *m/z*.

General procedure for CAHB-oxidation sequence with H_2O_2 (GP6).



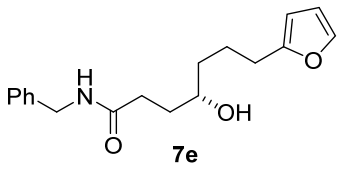
(*S*)-4-hydroxy-7-phenyl-heptanecarboxylic acid phenyl amide (7a). Following **GP4** with 0.5 mol% $[Rh(nbd)_2BF_4$/ 2(*R*)-**L1**] and **5a** (148 mg, 0.528 mmol) without purification, the resultant mixture was diluted with THF (10 mL) followed by addition of methanol (8 mL), sodium hydroxide (6 mL of a 3.0 M soln.), and the slow addition of H_2O_2 (1.0 mL of a 30% solution). The resulting mixture stirred (2 h) and then extracted with dichloromethane (3 x 15 mL). The combined organic extracts were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica gel (90:10-40:60 hexanes:ethyl acetate) affords the title compound (124 mg, 79%) as a white solid: m.p. 119.5–120.5 ºC; TLC analysis R_f 0.3 (40:60 hexanes:ethyl acetate); $[\alpha]_D^{20} = +7.5^o$ (*c* 1.0, MeOH); Chiral HPLC analysis (Chiralpak-IB, 70:30 hexanes:isopropanol, flow rate = 1.4 mL/min) showed peaks at 41 minutes (3.0% (*R*)) and 44 minutes (97.0% (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (1H, br s, NH), 7.51 (2H, d, *J* = 7.7 Hz, c,c'), 7.25–7.35 (4H, m, b,b',m,m'), 7.15–7.25 (3H, m, b,b',n,n',o), 7.12 (1H, t, *J* = 7.3 Hz, a), 3.60–3.80 (1H, m, h), 2.65 (2H, t, *J* = 7.8 Hz, k), 2.45–2.60 (3H, m, f, OH), 1.90–2.00 (1H, m, g), 1.70–1.85 (3H, m, g,j),

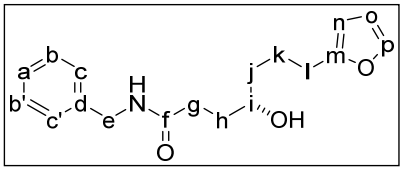
1.50–1.60 (2H, m, i); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.03 (e), 142.34 (l), 137.98 (d), 129.11 (b,b'), 128.53 (n,n'), 128.44 (m,m'), 125.90 (o), 124.43 (a), 120.02 (c,c'), 71.46 (h), 37.41 (i), 35.91 (k), 34.32 (f), 32.48 (g), 27.55 (j); IR (neat) 3670 (N-H stretch, O-H stretch), 3279, 3247, 2950, 2911, 1659 (C=O stretch), 1600 (N-H bend), 1543, 1496, 1412 (C-N stretch), 754, 689 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{23}NNaO_2$ (M+Na): 320.1626, found 320.1631 *m/z*.



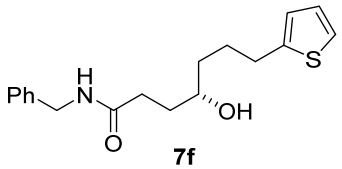
(*S*)-4-hydroxy-7-phenyl-4-heptanecarboxylic acid benzyl amide (7d). Following **GP6** with (*E*)-**5d** (155 mg, 0.528 mmol) affords, after flash chromatography on silica gel (80:20-20:80 hexanes:ethyl acetate), the title compound (131 mg, 80%) as a white solid: m.p. 88.5–89.5 ºC; TLC analysis R_f 0.4 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20} = -7.9^o$ (*c* 1.0, $CHCl_3$); Chiral HPLC analysis (Chiralpak-IC, 60:40 hexanes:isopropanol, flow rate = 1.3 mL/min) showed peaks at 28 minutes (3.5% (*R*)) and 32 minutes (96.5% (*S*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10–7.40 (10H, a,b,b',c,c',n,n',o,o',p), 6.28 (1H, br s, NH), 4.40 (2H, d, *J* = 5.7 Hz, e), 3.55–3.70 (1H, m, i), 3.19 (1H, d, *J* = 4.2 Hz, OH), 2.64 (2H, t, *J* = 7.6 Hz, l), 2.36 (2H, td, *J* = 7.3 and 2.8 Hz, g), 1.70–1.90 (2H, m, h,k), 1.60–1.70 (2H, m, h,k), 1.40–1.60 (2H, m, j); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.76 (f), 142.48 (m), 138.30 (d), 128.82 (b,b'), 128.54 (o,o'), 128.42 (n,n'), 127.89 (c,c'), 127.64 (a), 125.85 (p), 71.29 (i), 43.79 (e), 37.31 (j), 35.95 (l), 33.23 (g), 32.72 (h), 27.61 (k); IR (neat) 3306 (N-H stretch, O-H stretch), 3025, 2937, 2919, 2867, 1637 (C=O stretch), 1546 (N-H bend), 1495, 1442, 1234, 724, 694 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{25}NNaO_2$ (M+Na): 334.1783, found 334.1781 *m/z*.

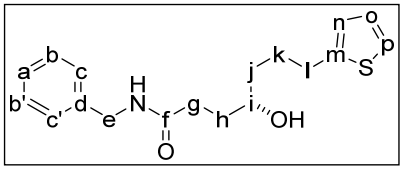
Following **GP6** with (*Z*)-**5d** (155 mg, 0.528 mmol) affords, after flash chromatography on silica gel (80:20-20:80 hexanes:ethyl acetate), the title compound (128 mg, 78%) as a white solid: m.p. 88.0–99.5 ºC; TLC analysis R_f 0.4 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20} = -7.8^o$ (*c* 1.0, $CHCl_3$); Chiral HPLC analysis (Chiralpak-IC, 60:40 hexanes:isopropanol, flow rate = 1.3 mL/min) showed peaks at 27 minutes (6.0% (*R*)) and 31 minutes (94.0% (*S*); spectroscopic data matched with (*S*)-**7d** obtained from (*E*)-**5d** as shown above.





(*S*)-7-(furan-2-yl)-4-hydroxyheptanecarboxylic acid benzyl amide (7e).[d] Following **GP6** with 1.0 mol% [Rh(nbd)$_2$BF$_4$/ 2(*R*)-**L1**] and **5e** (150 mg, 0.528 mmol) affords, after flash chromatography on silica gel (80:20-20:80 hexanes:ethyl acetate), the title compound (113 mg, 71%) as a light yellow solid: m.p. 72.5–74.0 ºC; TLC analysis R_f 0.35 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = –6.1º (*c* 2.0, $CHCl_3$); Chiral HPLC analysis (Chiralpak-IB, 60:40 hexanes:isopropanol, flowrate = 1.4 mL/min) showed peaks at 18 minutes (94.0% (*S*)) and 47 minutes (6.0% (*R*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.40 (6H, a,b,b',c,c',p), 6.29 (1H, dd, *J* = 2.9 and 2.0 Hz, o), 6.26 (1H, br s, NH, *overlapping with* o), 6.00 (1H, d, *J* = 3.0 Hz, n), 4.42 (2H, d, *J* = 5.7 Hz, e), 3.55–3.70 (1H, m, i), 2.85–3.45 (1H, br s, OH), 2.65 (2H, t, *J* = 7.4 Hz, l), 2.38 (2H, td, *J* = 7.2 and 3.4 Hz, g), 1.75–1.90 (2H, m, h,k), 1.60–1.75 (2H, m, h,k), 1.40–1.60 (2H, m, j); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.72 (f), 156.17 (m), 140.86 (p), 138.28 (d), 128.83 (b,b'), 127.90 (c,c'), 127.65 (a), 110.20 (o), 104.97 (n), 71.16 (i), 43.80 (e), 43.79 (e), 37.16 (j), 33.25 (g), 32.70 (h), 27.98 (l), 24.33 (k); IR (neat) 3288 (N-H stretch, O-H stretch), 2919, 1632 (C=O stretch), 1534, 1453, 1090, 1006, 723, 695 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{23}NNaO_3$ (M+Na): 324.1576, found 324.1573 *m/z*.



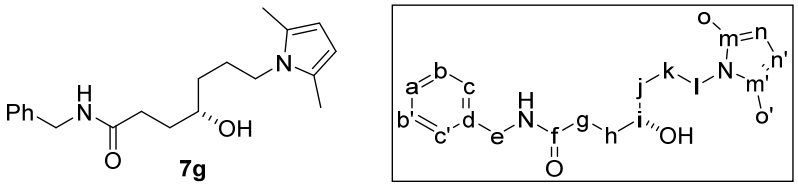


(*S*)-4-hydroxy-7-(thiophen-2-yl)-heptanecarboxylic acid benzyl amide (7f).[e] Following **GP6** with 1.0 mol% [Rh(nbd)$_2$BF$_4$/ 2(*R*)-**L1**] and **5f** (158 mg, 0.528 mmol) affords, after flash chromatography on silica gel (80:20-20:80 hexanes:ethyl acetate), the title compound (121 mg, 72%) as a white solid: m.p. 73.5–74.5 ºC; TLC analysis R_f 0.35 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = –4.7º (*c* 1.5, $CHCl_3$); Chiral HPLC analysis (Chiralpak-IB, 60:40 hexanes:isopropanol,

[d] A pseudo-racemate was prepared for HPLC analysis by combining crude reactions mixtures obtained by CAHB using (*R*)- and (*S*)-**L1** then oxidizing and isolating the resulting alcohol

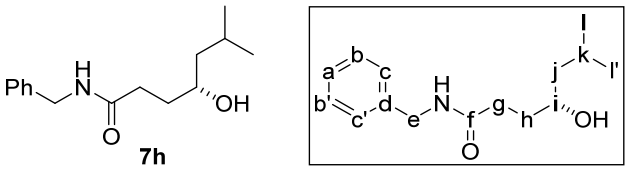
[e] A pseudo-racemate was prepared for HPLC analysis by combining crude reactions mixtures obtained by CAHB using (*R*)- and (*S*)-**L1** then oxidizing and isolating the resulting alcohol

flowrate = 1.4 mL/min) showed peaks at 28 minutes (94.0% (*S*)) and 109 minutes (6.0% (*R*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.40 (2H, b,b'), 7.25–7.35 (3H, a,c,c'), 7.12 (1H, dd, *J* = 5.1 and 1.0 Hz, p), 6.93 (1H, dd, *J* = 5.0 and 3.4 Hz, o), 6.80 (1H, dd, *J* = 3.3 and 0.8 Hz, n), 6.16 (1H, br s, NH), 4.43 (2H, d, *J* = 5.7 Hz, e), 3.60–3.70 (1H, m, i), 2.86 (2H, t, *J* = 7.5 Hz, l), 2.39 (2H, td, *J* = 7.2 and 3.8 Hz, g), 1.80–1.90 (2H, m, h,k), 1.65–1.80 (2H, m, h,k), 1.45–1.60 (2H, m, j); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.67 (f), 145.36 (m), 138.26 (d), 128.85 (b,b'), 127.92 (c,c'), 127.68 (a), 126.82 (o), 124.27 (n), 123.02 (p), 71.20 (i), 43.84 (e), 37.11 (j), 33.27 (g), 32.68 (h), 29.94 (l), 27.97 (k); IR (neat) 3291 (N-H stretch, O-H stretch), 2917, 2849, 1630 (C=O stretch), 1534, 1453, 691 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{23}NNaO_2S$ (M+Na): 340.1347, found 340.1354 *m/z*.



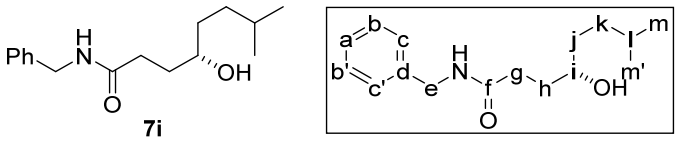
(*S*)-7-(2,5-dimethyl-1*H*-pyrrol-1-yl)-4-hydroxyheptanecarboxylic acid benzyl amide (7g).[f] Following **GP6** with 1.0 mol% [$Rh(nbd)_2BF_4$/ 2(*R*)-**L1**] and **5g** (164 mg, 0.528 mmol) affords, after flash chromatography on silica gel (80:20-20:80 hexanes:ethyl acetate), the title compound (102 mg, 59%) as a yellow oil; TLC analysis R_f 0.4 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = –7.1° (*c* 1.8, $CHCl_3$); Chiral HPLC analysis (Chiralpak-IC, 60:40 hexanes:isopropanol, flowrate = 1.4 mL/min) showed peaks at 42 minutes (8.0% (*R*)) and 54 minutes (92.0% (*S*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.40 (5H, a,b,b',c,c'), 6.10 (1H, br s, NH), 5.78 (2H, s, n,n'), 4.43 (2H, d, *J* = 5.7 Hz, e), 3.77 (2H, t, *J* = 7.6 Hz, l), 3.55–3.70 (1H, m, i), 2.30–2.45 (2H, m, g), 2.24 (6H, s, o,o'), 1.75–1.90 (2H, m, h,k), 1.65–1.75 (2H, m, h,k), 1.45–1.55 (2H, m, j); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.61 (f), 138.17 (d), 128.87 (b,b'), 127.92 (c,c'), 127.72 (a), 127.48 (m,m'), 105.19 (n,n'), 71.14 (i), 43.87 (e), 43.60 (l), 34.82 (j), 33.22 (g), 32.66 (h), 27.36 (k), 12.68 (o,o'); IR (neat) 3285 (N-H stretch, O-H stretch), 2923, 1643 (C=O stretch), 1541, 1453, 1407, 1298, 742, 697 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{28}N_2NaO_2$ (M+Na): 351.2048, found 351.2059 *m/z*.

[f] A pseudo-racemate was prepared for HPLC analysis by combining crude reactions mixtures obtained by CAHB using (*R*)- and (*S*)-**L1** then oxidizing and isolating the resulting alcohol



7h

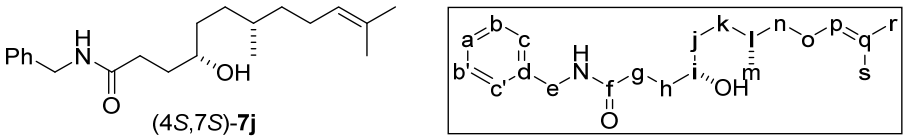
(*S*)-4-hydroxy-6-methylheptanecarboxylic acid benzyl amide (7h). Following **GP6** with **5h** (122 mg, 0.528 mmol) affords, after flash chromatography on silica gel (80:20-20:80 hexanes:ethyl acetate), the title compound (88 mg, 67%) as a white solid: m.p. 50.5–51.5 ºC; TLC analysis R_f 0.4 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20} = -18.4^o$ (*c* 2.0, $CHCl_3$); Chiral HPLC analysis (Chiralpak-IC, 90:10 hexanes:isopropanol, flowrate = 1.4 mL/min) showed peaks at 96 minutes (3.0% (*R*)) and 103 minutes (97.0% (*S*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.40 (2H, b,b'), 7.25–7.30 (3H, a,c,c'), 6.21 (1H, br s, NH), 4.43 (2H, d, *J* = 5.7 Hz, e), 3.65–3.75 (1H, m, i), 2.60–3.00 (1H, br s, OH), 2.40 (2H, td, *J* = 7.6 and 2.6 Hz, g), 1.80–1.90 (1H, m, h), 1.70–1.80 (1H, m, k), 1.60–1.70 (1H, m, h), 1.40–1.50 (1H, m, j), 1.20–1.25 (1H, m, j), 0.92 (6H, dd, *J* = 6.2 and 5.4 Hz, l,l'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.70 (f), 138.34 (d), 128.82 (b,b'), 127.89 (c,c'), 127.63 (a), 69.42 (i), 47.04 (j), 43.79 (e), 33.26 (h), 33.24 (g), 24.73 (k), 23.47 and 22.28 (l.l'); IR (neat) 3284 (N-H stretch, O-H stretch), 2952, 2916, 2868, 1643 (C=O stretch), 1546, 1453, 696 cm^{-1}; HRMS (ESI) calcd. for $C_{15}H_{23}NNaO_2$ (M+Na): 272.1626, found 272.1638 *m/z*.



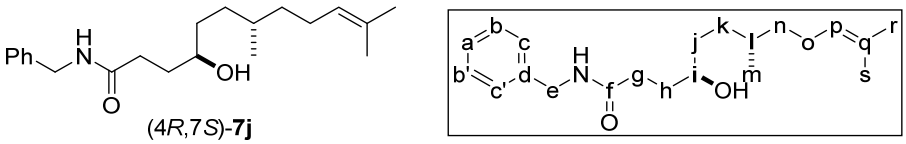
7i

(*S*)-4-hydroxy-7-methyloctanecarboxylic acid benzyl amide (7i). Following **GP6** with **5i** (130 mg, 0.528 mmol) affords, after flash chromatography on silica gel (80:20-20:80 hexanes:ethyl acetate), the title compound (104 mg, 75%) as a white solid: m.p. 61.0–62.0 ºC; TLC analysis R_f 0.4 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20} = -5.9^o$ (*c* 2.0, $CHCl_3$); Chiral HPLC analysis (Chiralcel-OD, 60:40 hexanes:isopropanol, flowrate = 1.0 mL/min) showed peaks at 11 minutes (96.5% (*S*)) and 16 minutes (3.5% (*R*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.35 (2H, b,b'), 7.20–7.30 (a,c,c'), 6.49 (1H, br s, NH), 4.39 (2H, d, *J* = 5.7 Hz, e), 3.50–3.60 (1H, m, i), 3.26 (1H, br s, OH), 2.30–2.45 (2H, m, g), 1.80–1.90 (1H, m, h), 1.60–1.70 (1H, m, h), 1.50–1.60 (1H, m, l), 1.40–1.50 (2H, m, j), 1.25–1.35 (1H, m, k), 1.15–1.25 (1H, m, k) 0.89 (6H, dd, *J* = 6.6 and 1.6 Hz, m,m'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.90 (f), 138.36 (d), 128.78 (b,b'), 127.84 (c,c'), 127.57 (a), 71.72 (i), 43.72 (e), 35.60 (j), 34.97 (k), 33.23 (g), 32.75 (h), 28.20 (l), 22.76

and 22.68 (m,m'); IR (neat) 3452 (N-H stretch), 3294 (O-H stretch), 2951. 2931, 2901, 2868, 1615 (C=O stretch), 1545, 1454, 1249, 1063, 1029, 723, 692 cm^{-1}; HRMS (ESI) calcd. for $C_{16}H_{25}NNaO_2$ (M+Na): 286.1783, found 286.1785 *m/z*.

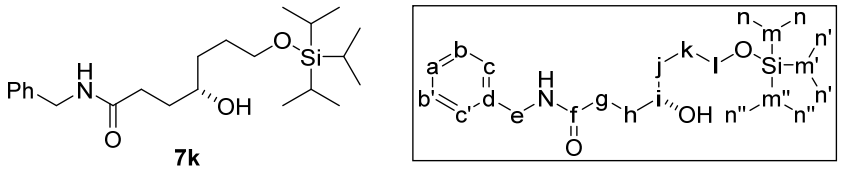


(4*S*,7*S*)-4-hydroxy-7,11-dimethyl-10-dodecenecarboxylic acid benzyl amide ((4*S*,7*S*)-7j). Following **GP6** with 1.0 mol% [Rh(nbd)$_2$BF$_4$/ 2(*R*)-**L1**] and **5j** (167 mg, 0.528 mmol) affords, after flash chromatography on silica gel (80:20-20:80 hexanes:ethyl acetate), the title compound (137 mg, 78%) as a white solid: m.p. 72.0–73.0 ºC; TLC analysis R_f 0.5 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20} = -2.5^o$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.40 (5H, a,b,b',c,c'), 6.30 (1H, br s, NH), 5.11 (1H, t, *J* = 5.8 Hz, p), 4.42 (2H, d, *J* = 5.5 Hz, e), 3.45–3.65 (1H, m, i), 3.05 (1H. br s, OH), 2.30–2.45 (2H, m, g), 1.80–2.05 (3H, m, o,h), 1.70 (3H, s, r), 1.62 (3H, s, s), 1.20–1.50 (6H, m, h,j,l,n), 1.15–1.20 (2H, m, k), 0.89 (3H, d, *J* = 5.5 Hz, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.77 (f), 138.33 (d), 131.19 (q), 128.80 (b,b'), 127.88 (c,c'), 127.61 (a), 125.01 (p), 71.92 (major diastereomer, 92%, i), 71.82 (minor diastereomer, 8%, i), 43.78 (e), 37.19 (minor diastereomer, 7%, l), 37.12 (major diastereomer, 93%, l), 35.29 (n), 33.26 (g), 32.99 (h), 32.65 (j and k *overlapping*), 25.83 (r), 25.64 (o), 19.67 (m), 17.77 (s); IR (neat) 3300 (N-H stretch, O-H stretch), 2962, 2911, 2849, 1642 (C=O stretch), 1552, 1452, 1344, 1256, 695 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{33}NNaO_2$ (M+Na): 354.2409, found 354.2414 *m/z*.

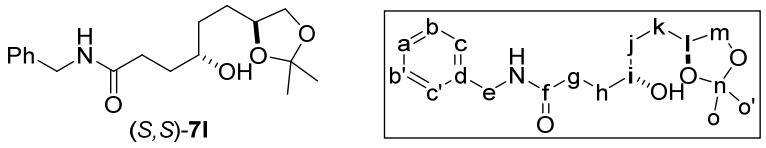


(4*R*,7*S*)-4-hydroxy-7,11-dimethyl-10-dodecenecarboxylic acid benzyl amide ((4*R*,7*S*)-7j). Following **GP6** with 1.0 mol% [Rh(nbd)$_2$BF$_4$/ 2(*S*)-**L1**] and **5j** (167 mg, 0.528 mmol) affords, after flash chromatography on silica gel (80:20-20:80 hexanes:ethyl acetate), the title compound (133 mg, 76%) as a white semi-solid; TLC analysis R_f 0.5 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20} = +6.5^o$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.35 (2H, m, b,b'), 7.25–7.30 (3H, m, a,c,c'), 6.30 (1H, br s, NH), 5.11 (1H, t, *J* = 6.2 Hz, p), 4.42 (2H, d, *J* = 5.7 Hz, e), 3.45–3.70 (1H, m, i), 3.04 (1H. br s, OH), 2.30–2.45 (2H, m, g), 1.80–2.05 (3H, m, o,h), 1.70 (3H, s, r), 1.62 (3H,

s, s), 1.20–1.50 (7H, m, h,j,k,l,n), 1.10–1.20 (1H, m, k), 0.89 (3H, d, J = 6.4 Hz, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.77 (f), 138.33 (d), 131.19 (q), 128.80 (b,b'), 127.88 (c,c'), 127.61 (a), 125.02 (p), 71.92 (minor diastereomer, 7%, i), 71.82 (major diastereomer, 93%, i), 43.78 (e), 37.19 (major diastereomer, 92%, l), 37.12 (minor diastereomer, 8%, l), 35.28 (n), 33.29 (g), 32.94 (h), 32.75 k), 32.58 (j), 25.83 (r), 25.65 (o), 19.61 (m), 17.77 (s); IR (neat) 3271 (N-H stretch, O-H stretch), 2912, 2851, 1651 (C=O stretch), 1616, 1538 1453, 727, 694 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{33}NNaO_2$ (M+Na): 354.2409, found 354.2412 *m/z*.

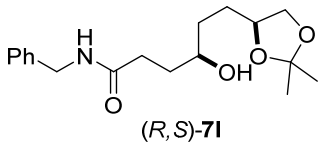


(*S*)-4-hydroxy-7((triisopropylsilyl)oxy)heptanecarboxylic acid benzyl amide (7k). Following **GP6** with **5k** (206 mg, 0.528 mmol) affords, after flash chromatography on silica gel (80:20-20:80 hexanes:ethyl acetate), the title compound (168 mg, 78%) as a colorless oil; TLC analysis R_f 0.4 (20:80 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = +7.1° (*c* 2.0, $CHCl_3$); Chiral HPLC analysis (Chiralpak-IC, 80:20 hexanes:isopropanol, flowrate = 1.4 mL/min) showed peaks at 29 minutes (3.0% (*R*)) and 35 minutes (97.0% (*S*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.35 (2H, b,b'), 7.25–7.30 (3H, a,c,c'), 6.28 (1H, br s, NH), 4.44 (2H, dd, J = 5.6 and 3.2 Hz, e), 3.70–3.85 (3H, m, l, OH), 3.60–3.70 (1H, m, i), 2.42 (2H, t, J = 7.0 Hz, g), 1.85–1.95 (1H, m, h), 1.60–1.80 (4H, m, h,j,k), 1.50–1.60 (1H, m, j), 1.00–1.15 (3H, m, m,m',m'', *overlapping with* n,n',n''), 1.08 (18H, s, n,n',n''); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.61 (f), 138.48 (d), 128.77 (b,b'), 127.88 (c,c'), 127.54 (a), 71.14 (i), 63.95 (l), 43.74 (e), 35.37 (j), 33.46 (g), 32.89 (h), 29.60 (k), 18.08 (n,n',n''), 12.02 (m,m',m''); IR (neat) 3289 (N-H stretch, O-H stretch), 2941, 2864, 1644 (C=O stretch), 1548, 1454, 1097, 881, 679 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{41}NNaO_3Si$ (M+Na): 430.2753, found 430.2763 *m/z*.

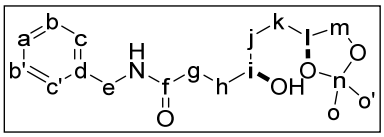


(*S*,*S*)-4-hydroxy-6-(2,2-dimethyl-1,3-dioxolan-4-yl)hexanecarboxylic acid benzyl amide ((*S*,*S*)-7l). Following **GP6** with 1.0 mol% [$Rh(nbd)_2BF_4$/ 2(*R*)-**L1**] and **5l** (160 mg, 0.528

mmol) affords, after flash chromatography on silica gel (70:30-0:100 hexanes:ethyl acetate), the title compound (122 mg, 72%) as a colorless oil; TLC analysis R_f 0.25 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = +10.1° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.35 (2H, m, b,b'), 7.25–7.30 (3H, m, a,c,c'), 6.27 (1H, br s, NH), 4.42 (2H, d, *J* = 5.7 Hz, e), 4.05–4.15 (1H, m, l), 4.05 (1H, dd, *J* = 6.0 and 6.0 Hz, m), 3.60–3.70 (1H, m, i), 3.53 (1H, dd, *J* = 7.5 and 7.5 Hz, m), 3.08 (1H. br s, OH), 2.40 (2H, t, *J* = 6.6 Hz, g), 1.80–1.90 (1H, m, h), 1.60–1.80 (3H, m, h,k), 1.50–1.60 (2H, m, j), 1.41 (3H, s, o,o'), 1.36 (3H, s, o,o'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.62 (f), 138.32 (d), 128.81 (b,b'), 127.87 (c,c'), 127.61 (a), 109.08 (n), 76.22 (l), 71.17 (major diastereomer, 96%, i), 71.02 (minor diastereomer, 4%, i), 69.56 (major diastereomer, 96%, m), 69.54 (minor diastereomer, 4%, m), 43.78 (e), 34.19 (major diastereomer, 95%, j), 34.01 (minor diastereomer, 5%, j), 33.28 (g), 32.86 (h), 30.23 (k), 27.01 (o,o'), 25.83 (o,o'); IR (neat) 3298 (N-H stretch, O-H stretch), 2984, 2932, 2868, 1644 (C=O stretch), 1543, 1454, 1369, 1214, 1155, 1053, 698 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{27}NNaO_4$ (M+Na): 344.1838, found 344.1847 *m/z*.

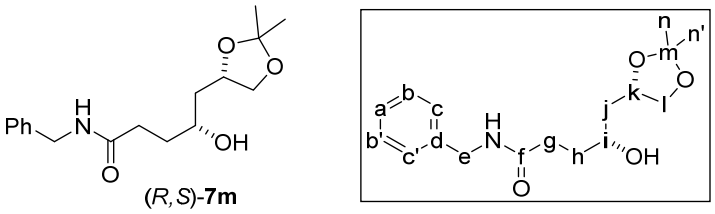


(*R,S*)-**7l**

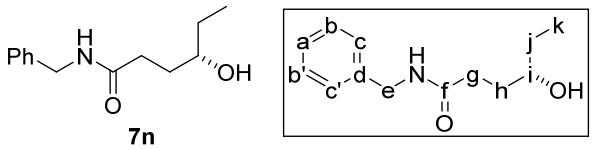


(*S,S*)-4-hydroxy-6-(2,2-dimethyl-1,3-dioxolan-4-yl)hexanecarboxylic acid benzyl amide ((*S,S*)-7l). Following **GP6** with 1.0 mol% [$Rh(nbd)_2BF_4$/ 2(*S*)-**L1**] and **5l** (160 mg, 0.528 mmol) affords, after flash chromatography on silica gel (70:30-0:100 hexanes:ethyl acetate), the title compound (122 mg, 72%) as a colorless oil; TLC analysis R_f 0.25 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = +22.3° (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.35 (2H, m, b,b'), 7.20–7.30 (3H, m, a,c,c'), 6.44 (1H, br s, NH), 4.39 (2H, d, *J* = 5.7 Hz, e), 4.05–4.15 (1H, m, l), 4.02 (1H, dd, *J* = 7.6 and 7.6 Hz, m), 3.55–3.75 (2H, m, i, OH), 3.50 (1H, dd, *J* = 7.2 and 7.2 Hz, m), 2.36 (1H, t, *J* = 6.0 Hz, g), 1.80–1.90 (1H, m, h), 1.55–1.80 (4H, m, h,j,k), 1.45–1.50 (1H, m, j), 1.40 (3H, s, o,o'), 1.35 (3H, s, o,o'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.68 (f), 138.28 (d), 128.75 (b,b'), 127.79 (c,c'), 127.55 (a), 108.93 (n), 76.21 (l), 71.06 (minor diastereomer, 5%, i), 70.95 (major diastereomer, 95%, i), 69.61 (minor diastereomer, 5%, m), 69.51 (major diastereomer, 95%, m), 43.69 (e), 34.19 (minor diastereomer, 0%, j), 33.94 (major diastereomer, 100%, j), 33.18 (g), 32.73 (h), 29.79 (k), 26.99 (o,o'), 25.79 (o,o'); IR (neat) 3294 (N-H stretch,

O-H stretch), 2984, 2931, 2869, 1644 (C=O stretch), 1542, 1454, 1369, 1214, 1054, 698 cm^{-1}; HRMS (ESI) calcd. for $C_{18}H_{27}NNaO_4$ (M+Na): 344.1838, found 344.1851 *m/z*.



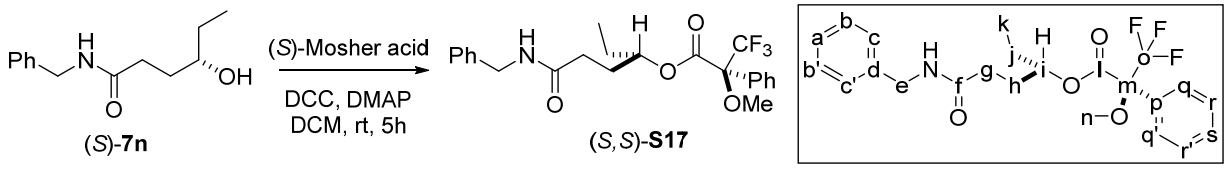
(*R*,*S*)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-4hydroxypentanecarboxylic acid benzyl amide ((*R*,*S*)-7m). Following **GP6** with 1.0 mol% [Rh(nbd)$_2$BF$_4$/ 2(*S*)-**L1**] and **5m** (153 mg, 0.528 mmol) affords, after flash chromatography on silica gel (70:30-0:100 hexanes:ethyl acetate), the title compound (114 mg, 70%) as a colorless oil; TLC analysis R_f 0.25 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20} = -3.5^o$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.35 (2H, m, b,b'), 7.20–7.30 (3H, m, a,c,c'), 6.37 (1H, br s, NH), 4.40 (2H, d, *J* = 5.7 Hz, e), 4.25–4.35 (1H, m, k), 4.07 (1H, dd, *J* = 8.0 and 6.1 Hz, l), 3.80–3.90 (1H, m, i), 3.55 (1H, dd, *J* = 7.8 and 7.8 Hz, l), 2.39 (1H, t, *J* = 6.9 Hz, g), 1.80–1.90 (1H, m, h), 1.60–1.80 (3H, m, h,j), 1.40 (3H, s, n,n'), 1.35 (3H, s, n,n'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.60 (f), 138.27 (d), 128.81 (b,b'), 127.86 (c,c'), 127.62 (a), 108.81 (m), 73.79 (k), 69.66 (major diastereomer, 92%, i), 69.49 (minor diastereomer, 8%, i), 68.58 (l), 43.77 (e), 40.67 (minor diastereomer, 7%, j), 40.56 (major diastereomer, 93%, j), 33.15 (g), 33.08 (h), 27.03 (n,n'), 25.78 (n,n'); IR (neat) 3304 (N-H stretch, O-H stretch), 2984, 2935, 2873, 1644 (C=O stretch), 1542, 1454, 1369, 1214, 1155, 1052, 698 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{25}NNaO_4$ (M+Na): 330.1681, found 330.1690 *m/z*.



(*S*)-4-hydroxy-hexanecarboxylic acid benzyl amide (7n). Following **GP6** with **5n** (107 mg, 0.528 mmol) affords, after flash chromatography on silica gel (80:20-20:80 hexanes:ethyl acetate), the title compound (71 mg, 61%) as a white solid: m.p. 63.5–64.5 ºC; TLC analysis R_f 0.4 (0:100 hexanes:ethyl acetate); $[\alpha]_D^{20} = +5.3^o$ (*c* 1.44, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20–7.40 (5H, a,b,b',c,c'), 6.48 (1H, br s, NH), 4.40 (2H, d, *J* = 5.2 Hz, e), 3.40–3.60 (1H, m, i), 3.21 (1H, br s, OH), 2.37 (2H, t, *J* = 6.5 Hz, g) 1.75–1.95 (1H, m, h), 1.55–1.75 (1H, m, h), 1.40–

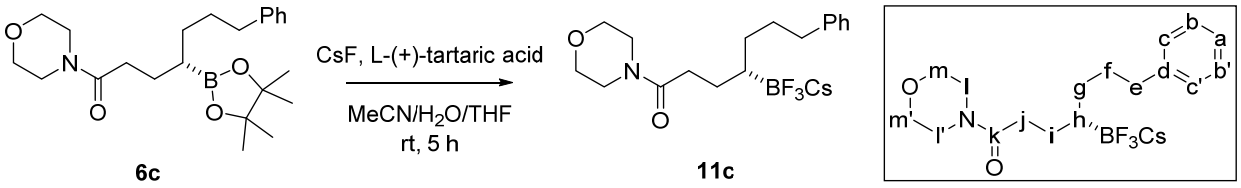
1.55 (2H, m, j), 0.93 (3H, t, J = 7.2 Hz, k); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.80 (f), 138.24 (d), 128.67 (b,b'), 127.74 (c,c'), 127.46 (a), 72.67 (i), 43.62 (e), 33.12 (g), 32.16 (h), 30.40 (j), 10.02 (k); IR (neat) 3280 (N-H stretch, O-H stretch), 2964, 2920, 2877, 1631 (C=O stretch), 1549 (N-H bend), 1493, 1326, 1264, 936, 729, 693 cm^{-1}; HRMS (ESI) calcd. for $C_{13}H_{19}NNaO_2$ (M+Na): 244.1313, found 244.1316 *m/z*.

Er of **7n** was determined by ^{19}F NMR of the corresponding Mosher ester (*S,S*)-**S17**.

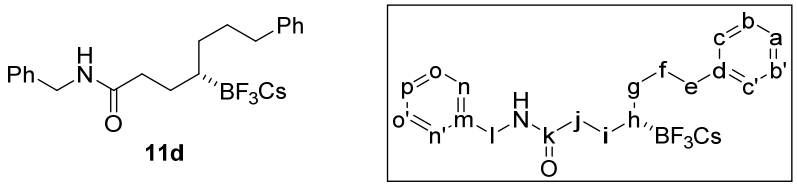


(*S*)-6-(benzylamino)-6-oxohexan-3-yl (*S*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoate ((*S,S*)-S17). To a solution of **7n** (0.06 mmol, 13.2 mg) and (*S*)-Mosher acid (3.1 equiv, 0.186 mmol, 44 mg) in DCM (1 mL) was added DCC (3.1 equiv, 0.186 mmol, 38.6 mg) and DMAP (3.1 equiv, 0.186 mmol, 22.8 mg). The resultant mixture was stirred at room temp for 5h then concentrated under vacuum. Flash column chromatography (80:20-50:50 hexanes:ethyl acetate) affords the title compound (24 mg, 92%) as a white semi-solid; TLC analysis R_f 0.5 (50:50 hexanes:ethyl acetate); $[\alpha]_D^{20} = -34.5^o$ (*c* 1.87, $CHCl_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ –71.01 (s, 5%, minor, CF_3), –71.08 (s, 95%, major, CF_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.60 (2H, m, r,r'), 7.25–7.45 (8H, a,b,b',c,c',q,q',s), 5.74 (0.94H, br s, major NH), 5.52 (0.05H, br s, minor NH), 5.00–5.15 (1H, m, i), 4.44 (2H, d, J = 5.7 Hz, e), 3.54 (3H, s, n), 2.05–2.30 (3H, m, g,h), 1.95–2.05 (1H, m, h), 1.60–1.70 (2H, m, j), 0.96 (0.12H, t, J = 7.4 Hz, minor k), 0.86 (2.89H, t, J = 7.4 Hz, major k); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.60 (f), 166.59 (l), 138.26 (d), 132.26 (p), 129.74 (r,r'), 128.85 (b,b'), 128.57 (q,q'), 127.98 (c,c'), 127.70 (s), 127.54 (a), 123.50 (q, J = 287 Hz, o), 84.79 and 84.52 (m), 78.16 (i), 55.47 (n), 43.82 (e), 32.21 (g), 29.38 (h), 26.82 (j), 9.37 (k); IR (neat) 3293 (N-H stretch), 2970, 2935, 1741 (C=O stretch), 1644 (C=O stretch), 1545 (N-H bend), 1452, 1258, 1165, 1121, 1016, 992, 715, 696 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{26}F_3NNaO_4$ (M+Na): 460.1712, found 460.1729 *m/z*.

General procedure for the preparation of cesium trifluoroborate salts (GP7).



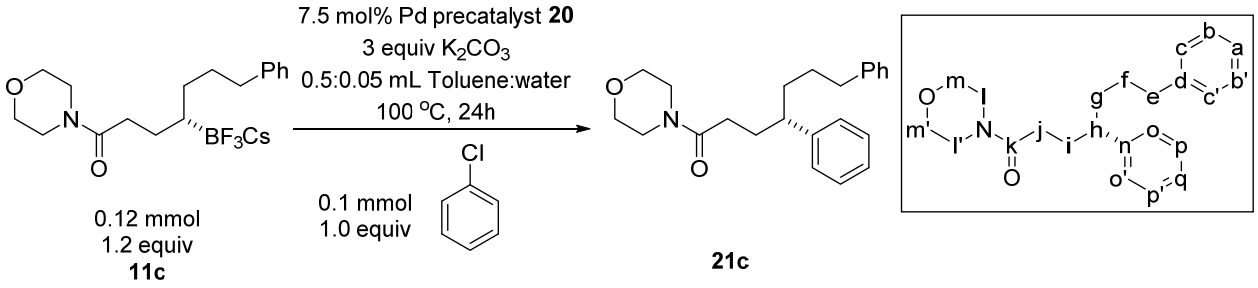
(*S*)-7-phenyl-4-(trifluoroborato)heptanecarboxylic acid morpholino amide, cesium salt (11c). To a solution of γ-dioxaborato amide **6c** (803 mg, 2.0 mmol, 1.0 equiv) in acetonitrile (MeCN, 8.0 mL) was added a solution of CsF (1.21 g, 8.0 mmol, 4.0 equiv) in H_2O (0.8 mL). The resultant mixture was stirred at room temp for 2 mins, and a solution of L-(+)-tartaric acid (614 mg, 4.1 mmol, 2.05 equiv) in THF (3.0 mL) was added dropwise. After a 5 h stir, the mixture was filtered, washed through with more MeCN, and the filtrate was concentrated under reduced pressure to afford the crude mixture of trifluorborate salt. Afterward, diethyl ether was added to the crude mixture to dissolve undesired products. Following a decantation to remove the solvent and undesired products, the precipitate was further dried under vacuum to afford the title compound (874 mg, 92%) as an off-white foamy solid: mp 61.5–62.5 ºC; $[\alpha]_D^{20}$ = +0.5º (*c* 1.0, $CHCl_3$); ^{19}F NMR (376 MHz, $CDCl_3$) δ –133.36 (s, BF_3Cs); ^1H NMR (400 MHz, $CDCl_3$) δ 7.25–7.30 (2H, m, b,b'), 7.15–7.20 (3H, m, a,c,c'), 3.55–3.60 (4H, m, m,m'), 3.45–3.55 (2H, m, l,l'), 3.30–3.40 (2H, m, l,l'), 2.58 (2H, t, *J* = 6.9 Hz, e), 2.25–2.35 (1H, m, j), 2.15–2.25 (1H, m, j), 1.50–1.70 (3H, m, f,i), 1.30–1.45 (2H, m, g,i), 1.10–1.25 (1H, m, g), 0.25–0.40 (1H, m, h); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.90 (k), 143.63 (d), 128.68 (b,b'), 128.39 (c,c'), 125.64 (a), 66.94 and 66.86 (m,m'), 46.28 and 41.86 (l,l'), 36.70 (e), 31.79 (j), 31.07 (f), 30.09 (g), 26.60 (i); IR (neat) 2908, 2854, 1609 (C=O stretch), 1461 (N-H bend), 1434, 1240 (C-N stretch), 1114, 1064, 957, 932, 742, 702 cm^{-1}; HRMS (ESI) calcd. for $C_{17}H_{24}BF_3NO_2$ (M-Cs): 342.1852, found 342.1852 *m/z*.



(*S*)-7-phenyl-4-(trifluoroborato)heptanecarboxylic acid benzyl amide, cesium salt (11d). Following **GP7** with γ-dioxaborato amide **6d** (421 mg, 1.0 mmol, 1.0 equiv) affords the title compound (396 mg, 80%) as a white foamy solid: mp 57.5–58.5 ºC; $[\alpha]_D^{20}$ = -2.9º (*c* 1.0, MeOH); ^{19}F NMR (376 MHz, MeOD) δ -131.52 (s, BF_3Cs); ^1H NMR (400 MHz, MeOD) δ 7.00–7.40 (10H, m, a,b,b',c,c',n,n',o,o',p), 4.36 (2H, s, l), 2.56 (2H, t, *J* = 7.7 Hz, e), 2.30 (2H, t, *J* = 8.1 Hz, j),

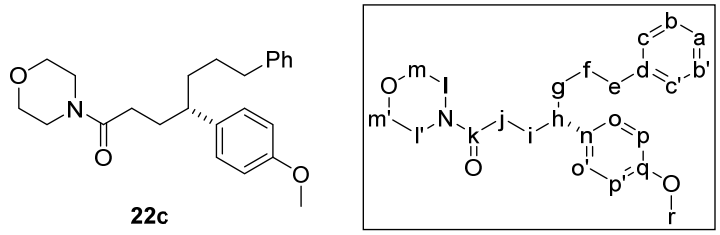
1.55–1.80 (4H, m, f,i), 1.40–1.55 (1H, m, g), 1.20–1.30 (1H, m, g), 0.30–0.50 (1H, m, h); ^{13}C NMR (100 MHz, MeOD) δ 177.08 (k), 143.66 (d), 138.97 (m), 128.16 (b,b'), 128.14 (o,o'), 127.76 (n,n'), 127.16 (c,c'), 126.74 (p), 124.94 (a), 42.67 (l), 36.67 (e), 36.01 (j), 31.06 (f), 30.79 (g), 27.83 (i); IR (neat) 3408 (N-H stretch), 3294 2919, 2852, 1640 (C=O stretch), 1521, 1495, 1452 (N-H bend), 1528, 912, 744, 697 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{24}BF_3NO$ (M-Cs): 362.1903, found 362.1897 *m/z*.

General procedure for Suzuki-Miyaura cross-coupling reactions (GP8).



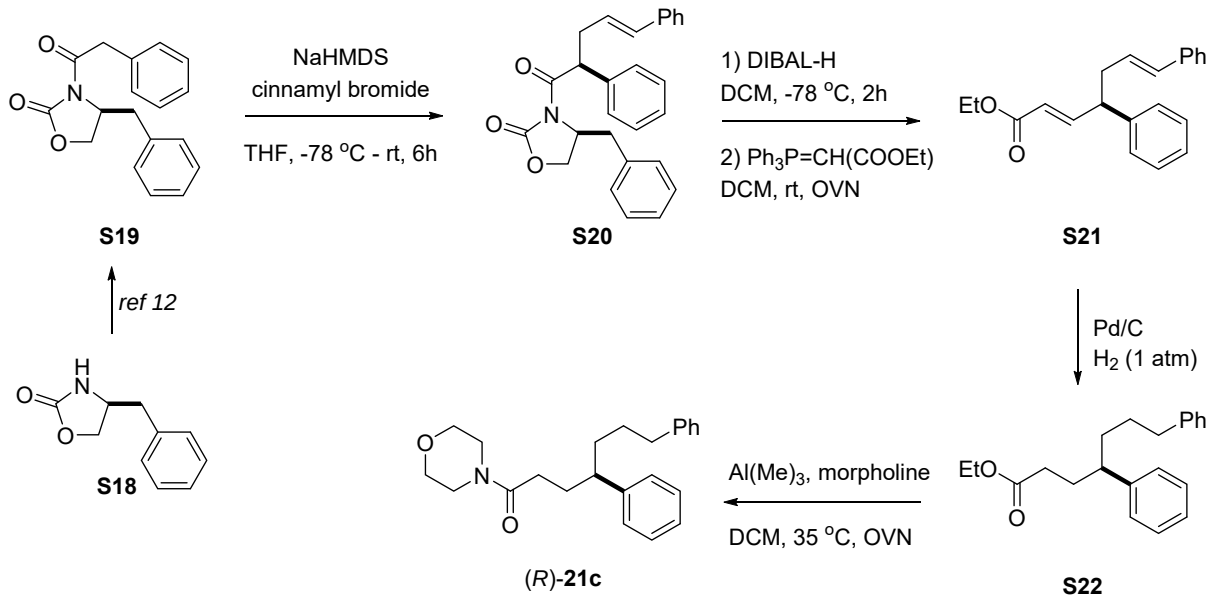
(*S*)-4,7-diphenylheptanecarboxylic acid morpholino amide ((*S*)-21c). An 8-mL vial was charged with Buchwald cataCXium® A Pd G3 precatalyst **20** (5.5 mg, 0.0075 mmol, 0.075 equiv), K_2CO_3 (42 mg, 0.3 mmol, 3.0 equiv), γ-trifluoroborato amide **11c** (57 mg, 0.12 mmol, 1.2 equiv), chlorobenzene (11.3 mg, 0.1 mmol, 1.0 equiv), toluene (0.5 mL), and water (0.05 mL). The resultant mixture was stirred at 100 °C for 24 h. After cooling to room temperature, the organic layer was separated, and water (1.0 mL) was added to the aqueous layer following by extraction with ethyl acetate (2 x 2 mL). The combined organic extracts were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica gel (95:5–80:20 DCM:ethyl acetate) affords the tile compound (22 mg, 63%) as a yellow oil; TLC analysis R_f = 0.4 (80:20 DCM:ethyl acetate); $[\alpha]_D^{20}$ = –3.7° (*c* 1.0, $CHCl_3$); Chiral HPLC analysis (Chiralpak-IC, 80:20 hexanes:isopropanol, flowrate = 1.5 mL/min) showed peaks at 75 minutes (6.5% (*R*)) and 81 minutes (93.5% (*S*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05–7.35 (10H, m, a,b,b',c,c',o,o',p,p',q), 3.50–3.65 (6H, m, l,l',m,m'), 3.10–3.30 (2H, m, l,l'), 2.50–2.65 (3H, m, e,h), 2.05–2.15 (3H, m, i,j), 1.80–1.90 (1H, m, i), 1.60–1.75 (2H, m, g), 1.45–1.60 (2H, m, f); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.72 (k), 144.84 (d), 142.55 (n), 128.60 (b,b'), 128.49 (p,p'), 128.33 (c,c'), 127.79 (o,o'), 126.42 (a), 125.74 (q), 67.01 and 66.67 (m,m'), 45.88 (l,l'), 45.61 (h), 41.95 (l,l'), 36.76 (g), 36.00 (e), 32.08 (i), 30.97 (j), 29.42 (f); IR (neat) 2919, 2851, 1644 (C=O stretch), 1452, 1426, 1230,

1114, 1029, 747, 699 cm^{-1}; HRMS (ESI) calcd. for $C_{23}H_{29}NNaO_2$ (M+Na): 374.2096, found 374.2106 *m/z*.



(*S*)-4-(4-methoxyphenyl)-7-phenylheptanecarboxylic acid morpholino amide (22c). Following **GP8** with 4-chloroanisole (14.3 mg, 0.1 mmol, 1.0 equiv) affords, after flash chromatography on silica gel (95:5–80:20 DCM:ethyl acetate), the title compound (19.8 mg, 52%) as a yellow oil; TLC analysis R_f 0.4 (80:20 DCM:ethyl acetate); $[\alpha]_D^{20} = -7.1^o$ (*c* 2.0, $CHCl_3$); Chiral HPLC analysis ((*S*,*S*)-WHELK-O 1, 50:50 hexanes:isopropanol, flow rate = 1.0 mL/min) showed peaks at 25 minutes (6.0% (*R*)) and 28 minutes (94.0% (*S*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (2H, t, *J* = 7.2 Hz, o,o'), 7.17 (1H, t, *J* = 7.3 Hz, a), 7.11 (2H, d, *J* = 7.1 Hz, c,c'), 7.06 (2H, d, *J* = 8.6 Hz, b,b'), 6.85 (2H, d, *J* = 8.6 Hz, p,p'), 3.81 (3H, s, r), 3.60–3.65 (2H, m, m,m'), 3.55–3.60 (4H, m, l,l',m,m'), 3.15–3.30 (2H, m, l,l'), 2.45–2.65 (3H, m, e,h), 2.00–2.15 (3H, m, i,j), 1.75–1.85 (1H, m, i), 1.45–1.75 (4H, m, f,g); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.80 (k), 158.12 (q), 142.60 (d), 136.77 (n), 128.61 (b,b'), 128.49 (c,c'), 128.32 (o,o'), 125.72 (a), 113.96 (p,p'), 67.02 and 66.69 (m,m'), 55.34 (r), 45.90 (l,l'), 44.76 (h), 41.95 (l,l'), 36.93 (g), 36.01 (e), 32.25 (i), 31.02 (j), 29.44 (f); IR (neat) 2920, 2852, 1643 (C=O stretch), 1510, 1426, 1244, 1113, 1030, 831, 700 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{31}NNaO_3$ (M+Na): 404.2202, found 404.2213 *m/z*.

<u>An allternative synthetic route for (*R*)-21c</u>



Compound **S19** was prepared as previously reported in literature.[12] To a cooled (-78 ºC) solution of **S19** (4.4 mmol, 1.3 g) in THF (15 mL) was added NaHMDS (1.1 equiv, 2M, 4.84 mmol, 2.4 mL) dropwise. The resultant mixture was stirred at -78 ºC for 1h, and cinnamyl bromide (2 equiv, 8.8 mmol, 1.73 g) was added dropwise. The resulting mixture was slowly warmed to room temp and stirred for another 5h before quenching with water. The crude reaction was extracted with EtOAc (3 x 30 mL). The organic extracts were combined, dried (anhyd. Na_2SO_4), and concentrated under reduced pressure. Flash chromatography on silica gel (75:25 hexanes:ethyl acetate) affords the tile compound **S20** (1.43 g, 79%) as a white solid: 143.5–144.5 ºC; TLC analysis R_f = 0.4 (70:30 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = +121º (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (2H, d, *J* = 7.3 Hz), 7.25–7.45 (10H, m), 7.15–7.25 (3H, m), 6.54 (1H, d, *J* = 15.8 Hz), 6.20–6.30 (1H, m), 5.33 (1H, dd, *J* = 9.0 and 6.2 Hz), 4.60–4.70 (1H, m), 4.00–4.20 (2H, m), 3.32 (1H, dd, *J* = 13.4 and 3.1 Hz), 3.05–3.20 (1H, m), 2.70–2.80 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.64, 153.11, 138.36, 137.42, 135.34, 132.76, 129.54, 129.05, 128.84, 128.77, 128.65, 127.67, 127.44, 127.38, 127.01, 126.26, 65.88, 55.80, 48.87, 38.02, 37.96; IR (neat) 3029, 1762 (C=O stretch), 1691 (C=O stretch), 1494, 1392, 1369, 1349, 1243, 1224, 1210, 1185, 1109, 1053, 984, 969, 743, 716, 700, 690 cm^{-1}; HRMS (ESI) calcd. for $C_{27}H_{25}NNaO_3$ (M+Na): 434.1732, found 434.1738 *m/z*.

To a cooled (-78 ºC) solution of **S20** (0.38 mmol, 156 mg) in DCM (2 mL) was added dropwise a solution of DIBAL-H (2 equiv, 1M, 0.76 mmol, 0.76 mL) dropwise. The resultant

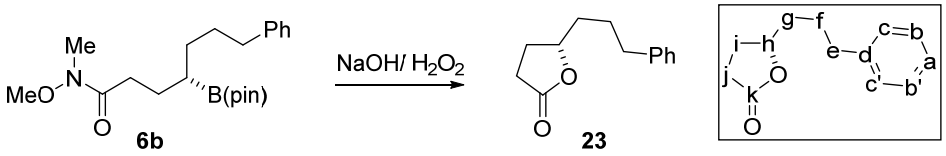
mixture was stirred at -78 °C for 2h. After quenching with satd. NH_4Cl (1 mL), the Wittig reagent (Ph_3P=CH(COOEt), 1.2 equiv, 0.456 mmol, 160 mg) in DCM (1 mL) was added dropwise. The resultant mixture was stirred OVN at room temp and passed through a pad of celite and washed with DCM (3 x 3 mL). The filtrate was concentrated under reduced pressure to give a crude **S21** (61.7 mg, 53%) used in the next step without further purification.

A solution of **S21** (0.18 mmol, 55 mg) and Pd/C (10%, 0.1 equiv) in methanol (1 mL) was stirred under H_2 (1 atm) for 5h. The resultant mixture was passed through a pad of celite and concentrated under reduced pressure to give a crude **S22** (55 mg, 99%) used in the next step without further purification.

Following **GP1** with **S22** (0.16 mmol, 50 mg) affords, after column chromatography (95:5–80:20 DCM:ethyl acetate), the title compound (*R*)-**21c** (40.2 mg, 71%) as a yellow oil; TLC analysis R_f = 0.4 (80:20 DCM:ethyl acetate); $[\alpha]_D^{20}$ = +3.2° (*c* 1.0, $CHCl_3$); (Chiralpak-IC, 80:20 hexanes:isopropanol, flowrate = 1.5 mL/min) showed peaks at 74 minutes (82.0% (*R*)) and 80 minutes (18.0% (*S*)); spectroscopic data matched with (*S*)-**21c** obtained from Suzuki-Miyaura cross-coupling of (*S*)-**11c.**

<u>Other stereospecific transformations of organoboranes</u>

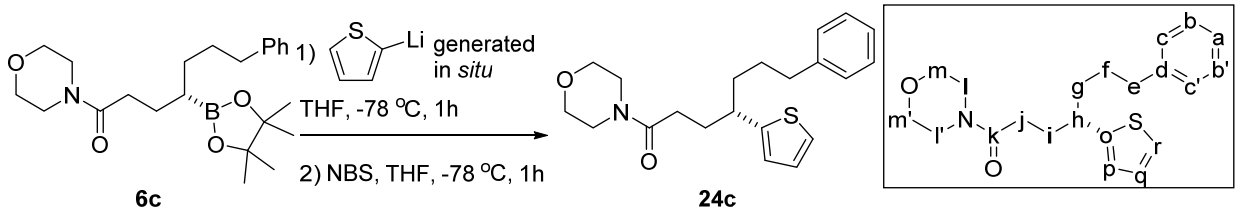
Formation of γ-lactone via harsh oxidation of γ-borylated Weinreb amide



(*S*)-5-(3-phenylpropyl)-γ-lactone (23). To a solution of γ-borylated Weinreb amide **6b** (0.264 mmol, 99 mg) in THF (5 mL) was added aq NaOH (3M, 4 mL) and H_2O_2 (0.5 mL of a 30% soln.). The resultant mixture was stirred for 2h at room temp. Sodium metabisulfite ($Na_2S_2O_5$, 3 mL of a 10% aq soln.) was added and the resultant mixture was stirred for another 15 mins before acidifying with HCl (6M). The resulting mixture was extracted with DCM (3 x 10 mL). The combined organic extracts were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica gel (75:25 hexanes:ethyl acetate) affords the title compound (51 mg, 95%) as a yellow oil; TLC analysis R_f 0.5 (75:25 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = -22.1° (*c*

1.04, $CHCl_3$); literature value +21.7° (*c* 1.04, $CHCl_3$) for the (*R*)-enantiomer;[13] spectroscopic data matched with literature:[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.35 (2H, b,b'), 7.15–7.25 (2H, a,c,c'), 4.45–4.60 (1H, m, h), 2.69 (2H, t, *J* = 6.9 Hz, e), 2.54 (2H, dd, *J* = 9.4 and 7.0 Hz, j), 2.25–2.40 (1H, m, i), 1.65–1.90 (5H, m, f,g,i); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.33 (k), 141.78 (d), 128.52 (b,b',c,c'), 126.08 (a), 80.95 (h), 35.59 (e), 35.20 (g), 28.94 (j), 28.10 (i), 27.14 (f). γ-lactone **23** was converting to 4-hydroxy benzyl amide **7d** following **GP1** to confirm the er.

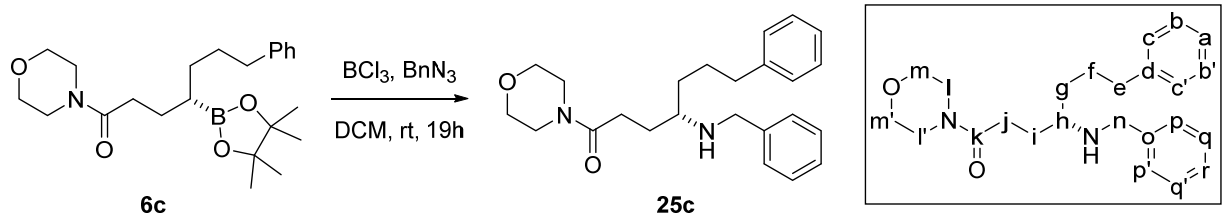
C(sp^3)–C(sp^2) coupling of boronic ester with thiophene using NBS[15]



(*S*)-7-phenyl-4-(thiophen-2-yl)heptanecarboxylic acid morpholino amide (24c). To a cooled (-78 °C) of thiophene (1.2 equiv, 0.3 mmol, 24 μL) in THF (1 mL) was added *n*-BuLi (1.2 equiv, 1.6M, 0.3 mmol, 0.19 mL) dropwise. The resultant mixture was allowed to warm to room temp and stirred for 1h. The reaction mixture was cooled to –78 °C again, and a solution of γ-borylated morpholino amide **6c** (0.25 mmol, 100 mg) in THF (0.5 ml) was added dropwise. The resulting mixture was stirred at the same temperature for 1h and a solution of NBS (1.2 equiv, 0.3 mmol, 54 mg) in THF (1 mL) was added dropwise. After 1h at –78 °C, satd. $Na_2S_2O_3$ (1 mL) was added and the reaction mixture was allowed to warm to room temp. The reaction mixture was diluted with EtOAc (10 mL) and water (5 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 10 mL). The combined organic extracts were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica gel (95:5–80:20 DCM:ethyl acetate) affords the title compound (75 mg, 84%) as a yellow oil; TLC analysis R_f = 0.4 (80:20 DCM:ethyl acetate); $[\alpha]_D^{20} = -9.1°$ (*c* 2.0, $CHCl_3$); Chiral HPLC analysis (Chiralcel-OJ-H, 100% isopropanol, flow rate = 1.0 mL/min) showed peaks at 12 minutes (5.5% (*R*)) and 18 minutes (94.5% (*S*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.30 (2H, m, c,c'), 7.10–7.20 (4H, m, a,b,b',r), 6.94 (1H, dd, *J* = 4.9 and 3.5 Hz, q), 6.79 (1H, d, *J* = 3.0, p), 3.55–3.70 (6H, m, l,l',m,m'), 3.25–3.35 (2H, m, l,l'), 2.90–3.00 (1H, m, h), 2.55–2.65 (2H, m, e), 2.10–2.25 (3H, m, i,j), 1.55–1.85 (5H, m, f,g,i); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.51 (k), 149.02 (o), 142.43 (d), 128.50

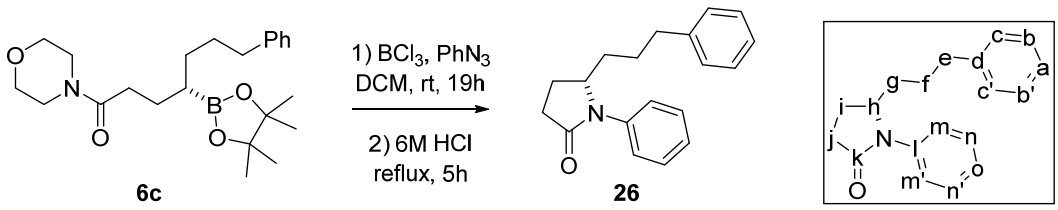
(b,b'), 128.37 (c,c'), 126.65 (q), 125.79 (a), 124.28 (p), 123.18 (r), 67.02 and 66.71 (m,m'), 45.92 and 41.99 (l,l'), 40.93 (h), 37.89 (g), 35.86 (e), 33.24 (i), 30.78 (j), 29.28 (f); IR (neat) 2920, 2853, 1642 (C=O stretch), 1452, 1429, 1229, 1113, 697 cm^{-1}; HRMS (ESI) calcd. for $C_{21}H_{27}NNaO_2S$ (M+Na): 380.1660, found 380.1678 *m/z*.

General procedure for BCl_3-assisted C–B to C–N bond formation (GP9)[16]



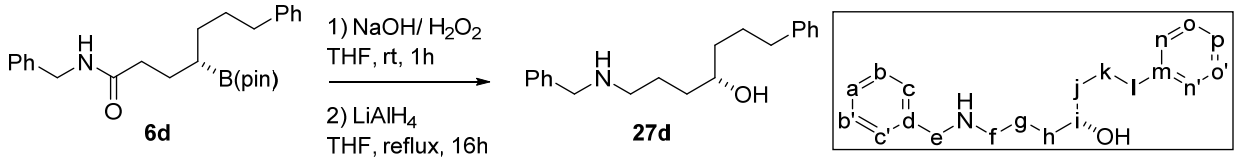
(*S*)-4-(benzylamino)-7-phenylheptanecarboxylic acid morpholino amide (25c). To a solution of BCl_3 (5 equiv, 1M, 0.5 mmol) in DCM was added dropwise at room temp a solution of γ-borylated morpholino amide **6c** (0.1 mmol, 40 mg) in DCM. After a 4h stir, the reaction mixture was carefully reduced under vacuum at room temp. It was then taken up in DCM (0.5 mL) and a solution of benzyl azide (3 equiv, 0.3 mmol, 40 mg) in DCM (0.2 mL) was added. The resultant mixture was stirred at room temp overnight and quenched with NaOH (2M). After extractions with DCM (3 x 5 mL), the combined organic extracts were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica gel (20:80-0:100 hexanes:acetone) affords the title compound (24.7 mg, 65%) as a yellow oil; TLC analysis R_f 0.2 (5:95 methanol:ethyl acetate); $[\alpha]_D^{20}$ = +7.5° (*c* 1.5, $CHCl_3$); Chiral HPLC analysis (Chiralcel-OJ-H, 90:10 hexanes:isopropanol, flow rate = 1.5 mL/min) showed peaks at 18 minutes (94.0% (*S*)) and 20 minutes (6.0% (*R*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.35 (7H, m, c,c',p,p',q,q',r), 7.15–7.25 (3H, a,b,b'), 3.70–3.80 (2H, m, n), 3.55–3.70 (6H, m, l,l',m,m'), 3.35–3.50 (2H, m, l,l'), 2.60–2.70 (3H, m, e,h), 2.36 (2H, t, *J* = 7.5 Hz, j), 1.80–1.90 (1H, m, i), 1.60–1.80 (1H, m, f,i), 1.45–1.60 (2H, m, g); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.10 (k), 142.40 (d), 140.76 (o), 128.55 (b,b'), 128.51 (q,q'), 128.43 (c,c'), 128.28 (p,p'), 127.06 (r), 125.89 (a), 67.04 and 66.76 (m,m'), 56.17 (h), 50.99 (n), 46.03 and 42.03 (l,l'), 36.07 (e), 33.47 (g), 29.02 (j), 28.99 (i), 27.64 (f); IR (neat) 2934, 2854, 1640 (C=O stretch), 1452, 1430, 1114, 746, 698 cm^{-1}; HRMS (ESI) calcd. for $C_{24}H_{32}N_2NaO_2$ (M+Na): 403.2361, found 403.2363 *m/z*.

Formation of γ-lactam via C–B to C–N formation followed by acidic removal of morpholino amide



(*S*)-*N*-phenyl-3-(phenylpropyl)-γ-lactam (26). Following **GP9** with phenyl azide (3 equiv, 0.3 mmol, 36 mg) affords the corresponding amine, which was then taken up in HCl (6M, 1 mL). After 6h reflux, the reaction mixture was cooled to room temp and extracted with DCM (3 x 2 mL). The combined organic extracts were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica gel (80:20-40:60 hexanes:ethyl acetate) affords the title compound (19 mg, 68%) as a yellow liquid; TLC analysis R_f 0.4 (40:60 hexanes:ethyl acetate); $[\alpha]_D^{20}$ = +30.5° (*c* 0.74, $CHCl_3$); Chiral HPLC analysis ((*S*,*S*)-WHELK-O 1, 100% isopropanol, flow rate = 1.0 mL/min) showed peaks at 9 minutes (5.5% (*R*)) and 17 minutes (94.5% (*S*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.45 (4H, m, m,m',n,n'), 7.20–7.30 (4H, m, a,b,b',o), 7.12 (2H, d, *J* = 7.2 Hz, c.c'), 4.30–4.30 (1H, m, h), 2.50–2.70 (4H, m, e,j), 2.30–2.40 (1H, m, i), 1.80–1.90 (1H, m, i), 1.55–1.80 (3H, m, f,g), 1.40–1.50 (1H, m, g); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.46 (k), 141.83 (d), 137.71 (l), 129.15 (n,n'), 128.50 (b,b'), 128.36 (c,c'), 126.06 (o), 126.00 (a), 124.32 (m,m'), 59.78 (h), 35.71 (e), 33.08 (g), 31.41 (j), 26.50 (f), 24.07 (i); IR (neat) 2933, 1690 (C=O stretch), 1596, 1496, 1388, 1292, 1220, 752, 693 cm^{-1}; HRMS (ESI) calcd. for $C_{19}H_{21}NNaO$ (M+Na): 302.1521, found 302.1534 *m/z*.

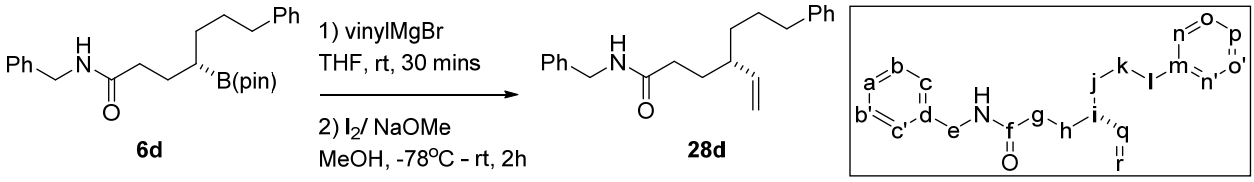
Formation of 1,4-aminoalcohol via oxidation of C–B bond followed by amide reduction with $LiAlH_4$



(*S*)-1-(benzylamino)-7-phenyl-4-heptanol (27d). To a solution of γ-borylated benzyl amide **6d** (0.3 mmol, 127 mg) in THF (5 mL) was added aq NaOH (3M, 6 mL) and H_2O_2 (0.8 mL

of a 30% soln.). The resultant mixture was stirred for 1h at room temp. After extraction with DCM and concentration under reduced pressure, without further purification, the obtained residue (crude **7d**) was taken up with THF (1.5 mL). To the cooled (0 ºC) resultant mixture was added $LiAlH_4$ (2 equiv, 0.6 mmol, 23 mg). The reaction mixture was refluxed overnight. After cooling to room temp, the resulting mixture was quenched with KOH (5M, 0.05 mL) and water (0.05 mL) followed by 30-min stir. The reaction mixture was then filtered through a pad of celite and washed with EtOAc (3 x 2 mL). The filtrate was concentrated under reduced pressure. Flash chromatography on silica gel (50:50-0:100 hexanes:acetone) affords the title compound (84 mg, 94%) as a light yellow solid: m.p. 48.5–49.0 ºC; TLC analysis R_f 0.2 (5:95 methanol:ethyl acetate); $[\alpha]_D^{20} = +20.4^o$ (*c* 2.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20–7.40 (10H, a,b,b',c,c',n,n',o,o',p), 3.80 (2H, d, *J* = 1.9 Hz, e), 3.40–3.70 (2H, m, i,OH), 2.75–2.85 (1H, m, f), 2.67 (2H, t, *J* = 7.7 Hz, l), 2.55–2.65 (1H, m, f), 1.65–1.90 (4H, m, h,k), 1.40–1.60 (4H, m, g,j); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.85 (m), 139.41 (d), 128.69 (b,b'), 128.58 (o,o'), 128.45 (n,n'), 127.35 (c,c'), 127.37 (a), 125.72 (p), 71.33 (i), 53.98 (e), 49.57 (f), 37.51 (j), 37.19 (h), 36.20 (l), 27.97 (k), 27.41 (g); IR (neat) 3267 (N-H stretch, O-H stretch), 3084, 3026, 2868, 2827, 2813, 1495, 1451, 1363 (C-N stretch), 1346, 1118, 858, 734, 691 cm^{-1}; HRMS (ESI) calcd. for $C_{20}H_{27}NNaO$ (M+Na): 320.1990, found 320.1990 *m/z*.

Vinylation of boronic ester using vinylmagnesium bromide[17]



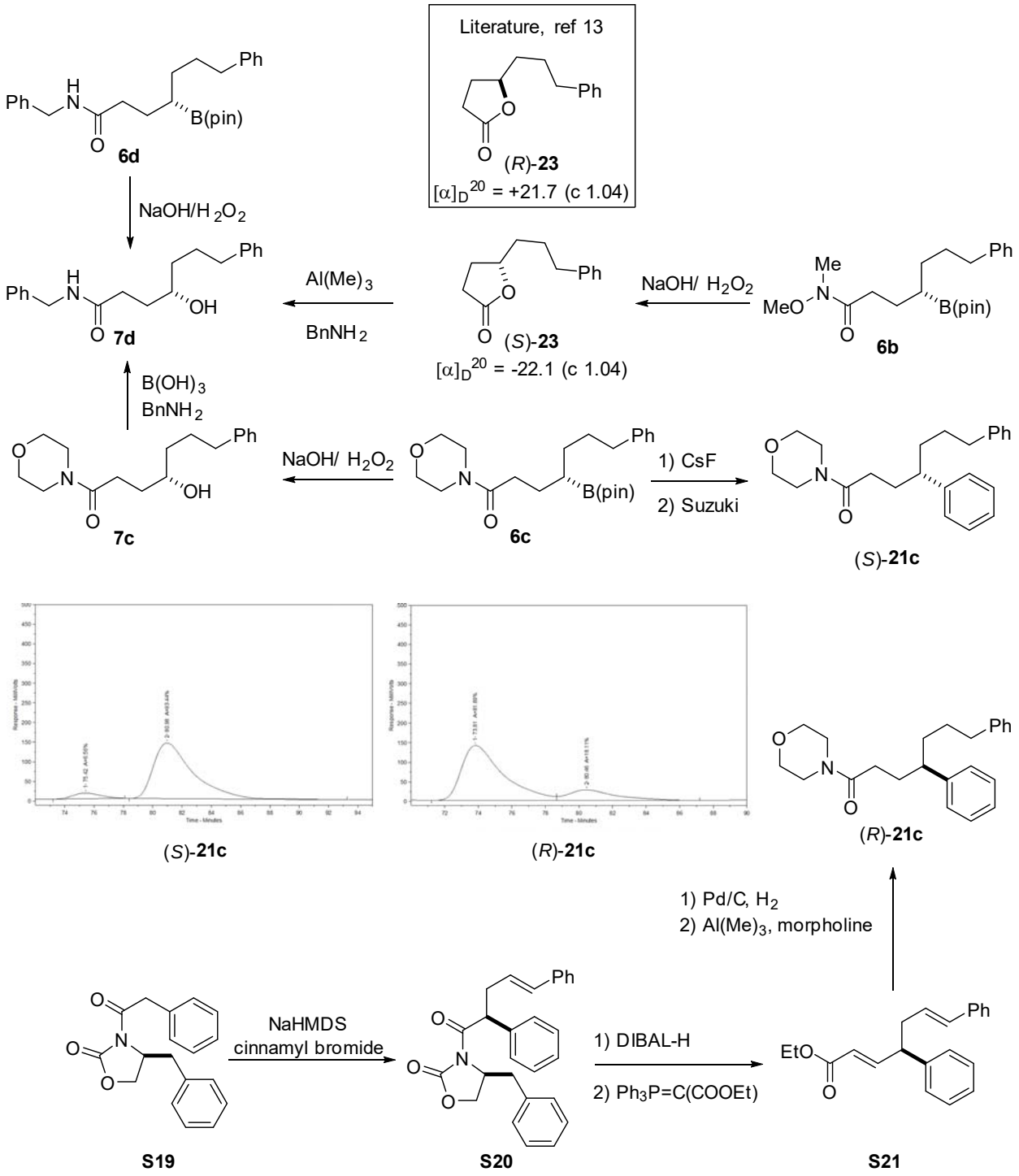
(*S*)-7-phenyl-4-vinylheptanecarboxylic acid benzyl amide (28d). To ad solution of γ-borylated benzyl amide **6d** (0.15 mmol, 63 mg) in THF (1.5 mL) was added vinylmagnesium bromide (4 equiv, 1M, 0.6 mmol, 0.6 mL) dropwise. The resultant mixture was stirred as room temp for 30 mins. To the above solution at-78 ºC was added iodine (4 equiv, 0.6 mmol, 152 mg) in methanol (2.0 mL) dropwise. The reaction mixture was allowed to stir 30 mins at the same temp followed by dropwise addition of a solution of NaOMe (8 equiv, 1.2 mmol, 65 mg) in methanol (2.5 mL). After warming to room temp, the resultant mixture was stirred for another 1.5h. It was then diluted with pentane (20 mL) and wash sequentially with 10% aqueous soln. of $Na_2S_2O_3$ (5 mL) and water (5 mL). The organic layer was separated and the aqueous layer was washed with

pentane (2 x 10 mL). The combined organic layers were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. Flash chromatography on silica gel (80:20-60:40 hexanes:ethyl acetate) affords the title compound (45 mg, 93%) as a colorless oil; TLC analysis R_f 0.5 (50:50 hexanes:ethyl acetate); $[\alpha]_D^{20} = -4.1^o$ (*c* 2.0, $CHCl_3$); Chiral HPLC analysis (Chiralcel-OJ-H, 90:10 hexanes:isopropanol, flow rate = 1.0 mL/min) showed peaks at 18 minutes (4.0% (*R*)) and 22 minutes (96.0% (*S*)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.40 (2H, m, b,b'), 7.25–7.35 (5H, a, n,n',o,o'), 7.15–7.25 (3H. c,c',p), 5.76 (1H, br s, NH), 5.50 (1H, dt, *J* = 17.0 and 9.6 Hz, q), 5.02 (1H, dd, *J* = 10.1 and 1.6 Hz, r), 4.96 (1H, dd, *J* = 17.1 and 1.5 Hz, r), 4.45 (2H, dd, *J* = 5.1 and 4.0 Hz, e), 2.50–2.70 (2H, m, l), 2.20–2.30 (1H, m, g), 2.10–2.20 (1H, m, g), 1.95–2.10 (1H, m, i), 1.80–1.90 (1H, m, k), 1.50–1.75 (3H, m, h,k), 1.40–1.50 (1H, m, j), 1.30–1.40 (1H, m, j); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.96 (f), 142.72 (q), 142.36 (m), 138.54 (d), 128.83 (o,o'), 128.53 (b,b'), 128.38 (n,n'), 127.98 (c,c') 127.63 (a), 125.76 (p), 115.58 (r), 43.96 (i), 43.71 (e), 36.03 (l), 34.77 (j), 34.59 (g), 30.69 (k), 29.13 (h); IR (neat) 3275 (N-H stretch), 3063, 3027, 2925, 2856, 1641 (C=O stretch), 1541, 1495, 1453, 911, 745, 696 cm^{-1}; HRMS (ESI) calcd. for $C_{22}H_{27}NNaO$ (M+Na): 344.1990, found 344.1996 *m/z*.

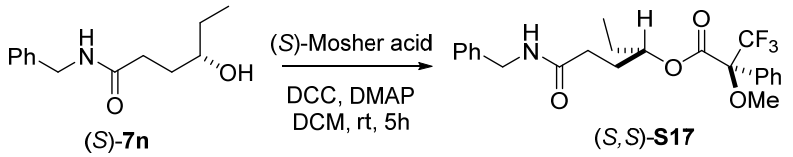
Determination of absolute configurations (Detailed procedures described above.)

γ-Borylated carbonyl derivatives **6b-d** were obtained by CAHB of **5b-d** using (*R*)-**L1** as described above. Treatment of **6b** with NaOH/ H_2O_2 generated an enantiomer of a known lactone (*R*)-**23**. The opposite sign of optical rotation showed that CAHB products are (*S*)-enantiomers. To further confirm the assignment, (*S*)-**23** and (*S*)-**7c** were converted to (*S*)-**7d** resulting in the same order of elution in HPLC (traces shown below, *vide infra*).

To determine the Suzuki-Miyaura product configuration, authentic (*R*)-**21c** was prepared via Evan's chiral auxiliary enolate allylation, *in situ* half reduction to aldehyde followed by Wittig reaction, Pd/C hydrogenation and morpholine transamidation. Though **S20** is not known in literature, allylation[18,19] and benzylation[12] of **S19** were reported in the same sense of diastereoselectivity. HPLC traces of authentic (*R*)-**21c** and **21c** obtained from Suzuki-Miyaura cross-coupling of **6c** (after converting to trifluoroborate **11c**) showed that they are enantiomers indicating the Suzuki product was (*S*)-enantiomers. Starting from (*S*)-**6c** to obtain (*S*)-**21c** leads to a conclusion of stereoretentive Suzuki-Miyaura cross-coupling.

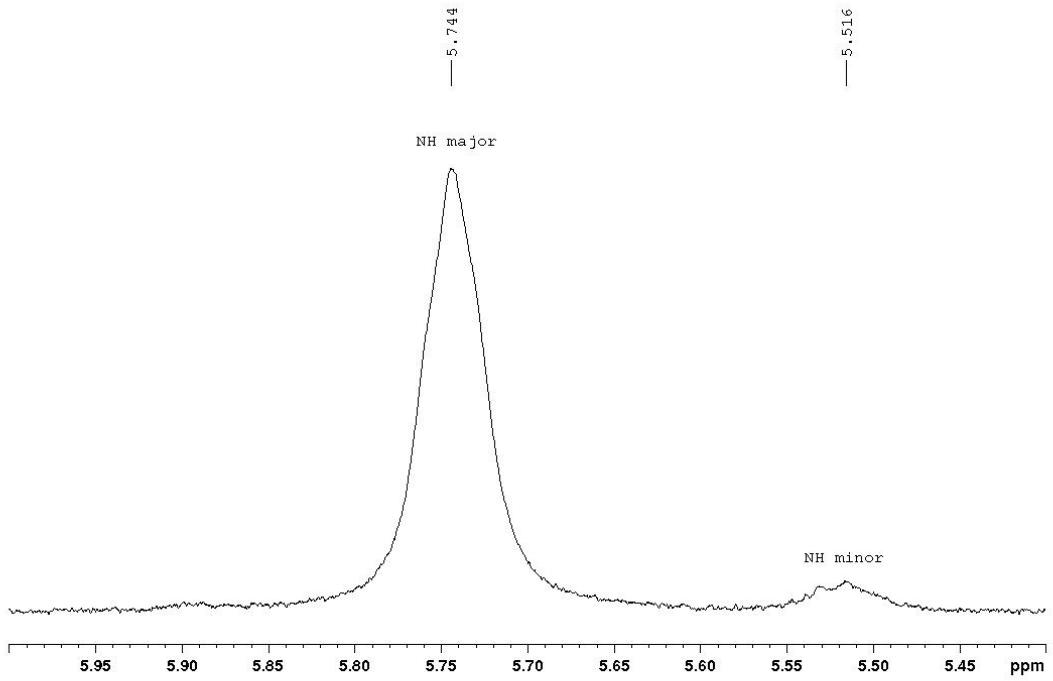


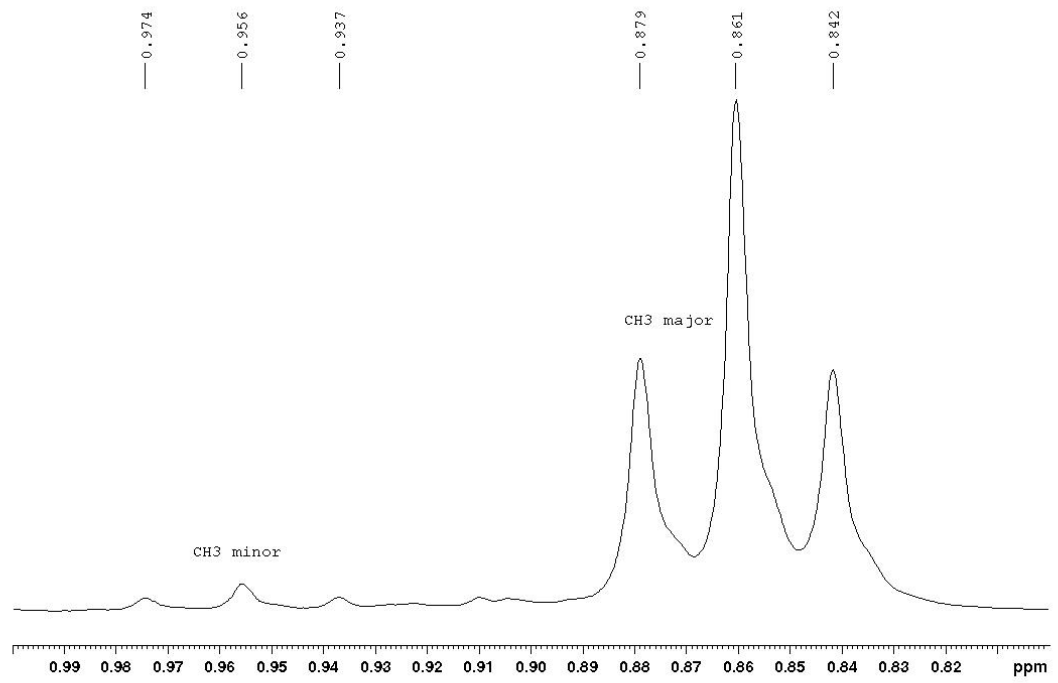
An alternative method for determination of absolute configurations of CAHB products



(*S*)-**7n** (*S,S*)-**S17**

The two figures below are the ^{1}H NMR regions of NH and methyl groups of Mosher ester **S17,** prepared from **7n** (obtained from CAHB of **5n** with (*R*)-**L1**, *vide supra*) and (*S*)-Mosher acid, respectively. From the figures, the major NH is more downfield, whereas, the major methyl group is more upfield. According to Feng Shao's[20] protocol for determination of absolute configuration using Mosher ester analysis, the NH is on the same side of the methoxy group and the methyl group is on the opposite side of the methoxy group resulting in *S,S*-configuration of **S17**. The method might not be reliable for determining absolute configuration of **S17** by itself since both NH and methyl groups are quite far away from the Mosher ester chiral center. However, the result is consistent with correlation to the known lactone **23** as described above.


5.744
5.516
NH major
NH minor
5.95 5.90 5.85 5.80 5.75 5.70 5.65 5.60 5.55 5.50 5.45 ppm


0.974
0.956
0.937
0.879
0.861
0.842
CH3 major
CH3 minor
0.99 0.98 0.97 0.96 0.95 0.94 0.93 0.92 0.91 0.90 0.89 0.88 0.87 0.86 0.85 0.84 0.83 0.82 ppm

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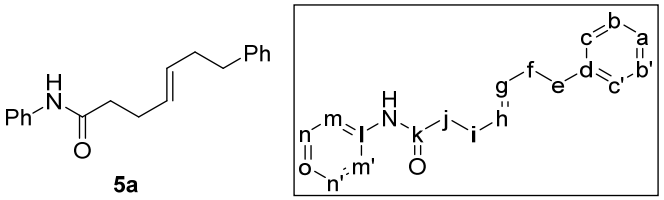
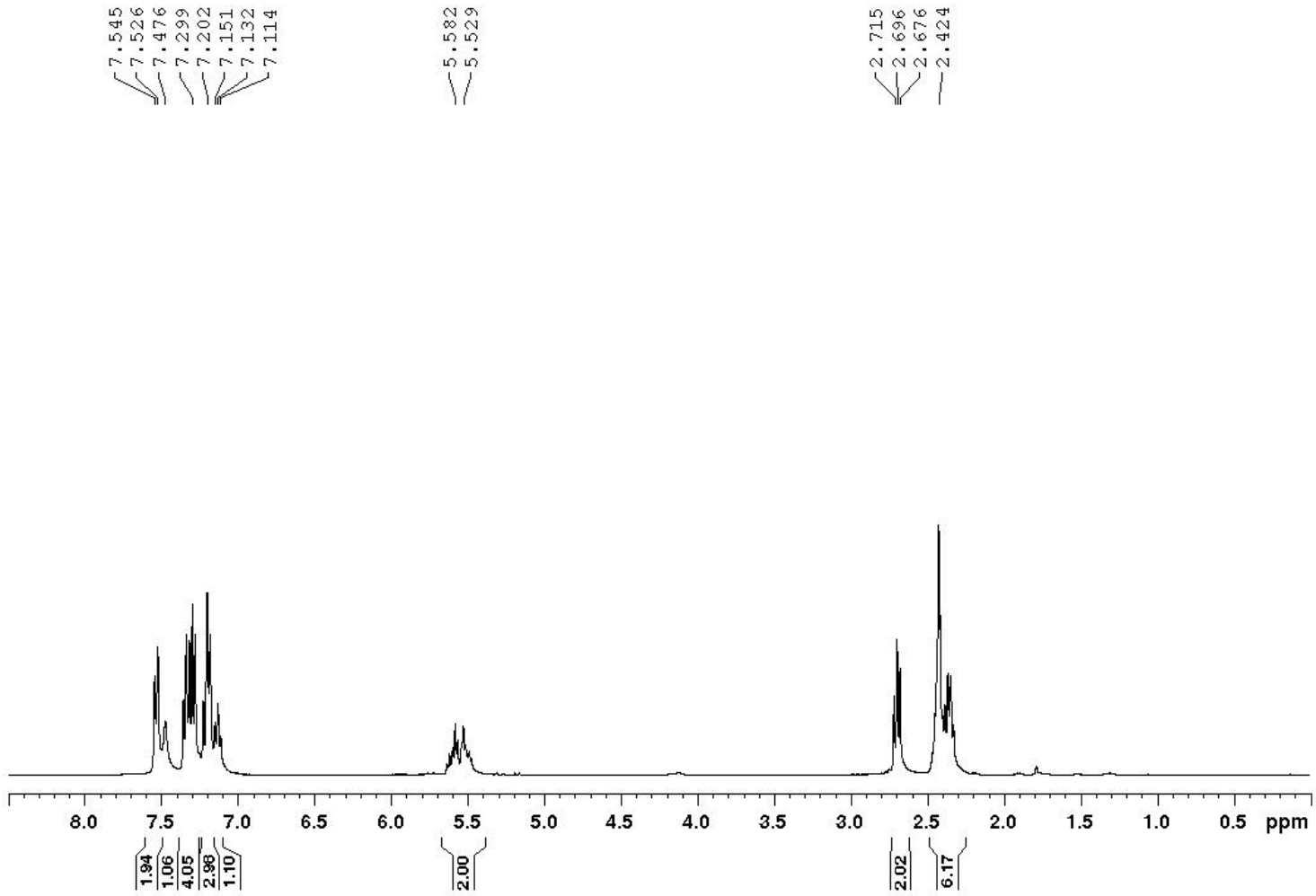
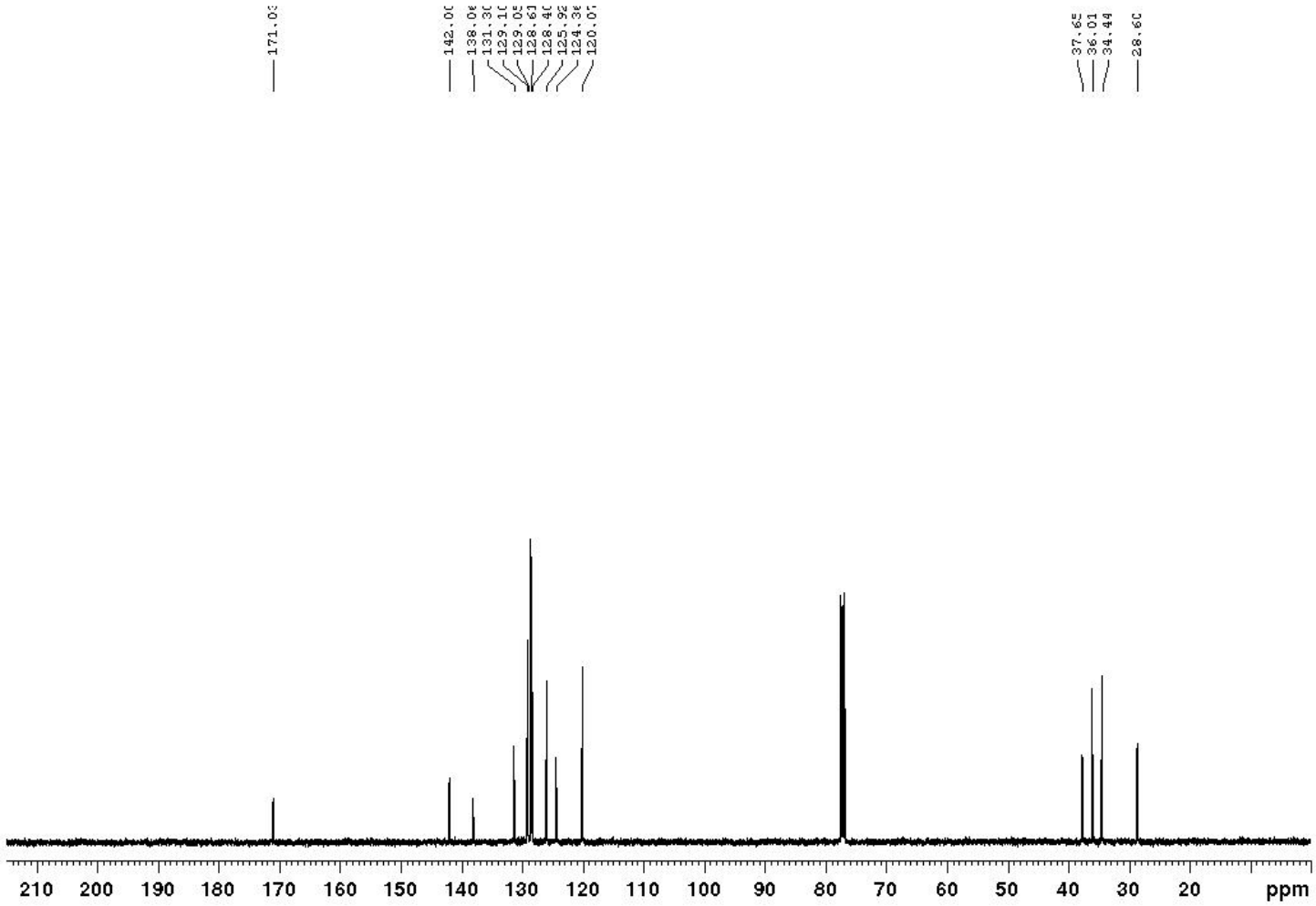


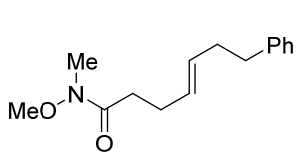
m.p.	106.0–107.0 ºC
TLC analysis	R_f 0.65 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.54 (2H, d, *J* = 7.8 Hz, m,m'), 7.48 (1H, br s, NH), 7.25–7.40 (4H, m, b,b',n,n'), 7.15–7.25 (3H, m, c,c',a), 7.13 (1H, t, *J* = 7.4 Hz, o), 5.40–5.70 (2H, m, g,h), 2.70 (2H, t, *J* = 7.4 Hz, e), 2.25–2.50 (6H, m, f,i,j)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 171.03 (k), 142.00 (d), 138.06 (l), 131.30 (h), 129.10 (g), 129.05 (n,n'), 128.61 (b,b'), 128.40 (o), 125.92 (c,c'), 124.36 (a), 120.07 (m,m'), 37.65 (e), 36.01 (j), 34.44 (f), 28.60 (i)
IR (neat)	3305 (N-H stretch), 3265, 2193, 1664 (C=O stretch), 1603, 1546, 1439, 972, 757, 693 cm^{-1}
HRMS (ESI)	$C_{19}H_{21}NNaO$ (M+Na): 302.1521, found 302.1531 *m/z*

^{1}H NMR of 5a

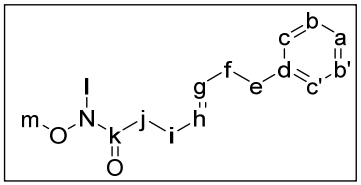

7.545
7.526
7.476
7.299
7.202
7.151
7.132
7.114
5.582
5.529
2.715
2.696
2.676
2.424
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.94
1.06
4.05
2.98
1.10
2.00
2.02
6.17

^{13}C NMR of 5a


171.0
142.0
138.0
131.3
129.1
129.0
128.6
128.4
125.9
124.3
120.0
37.65
36.01
34.49
28.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

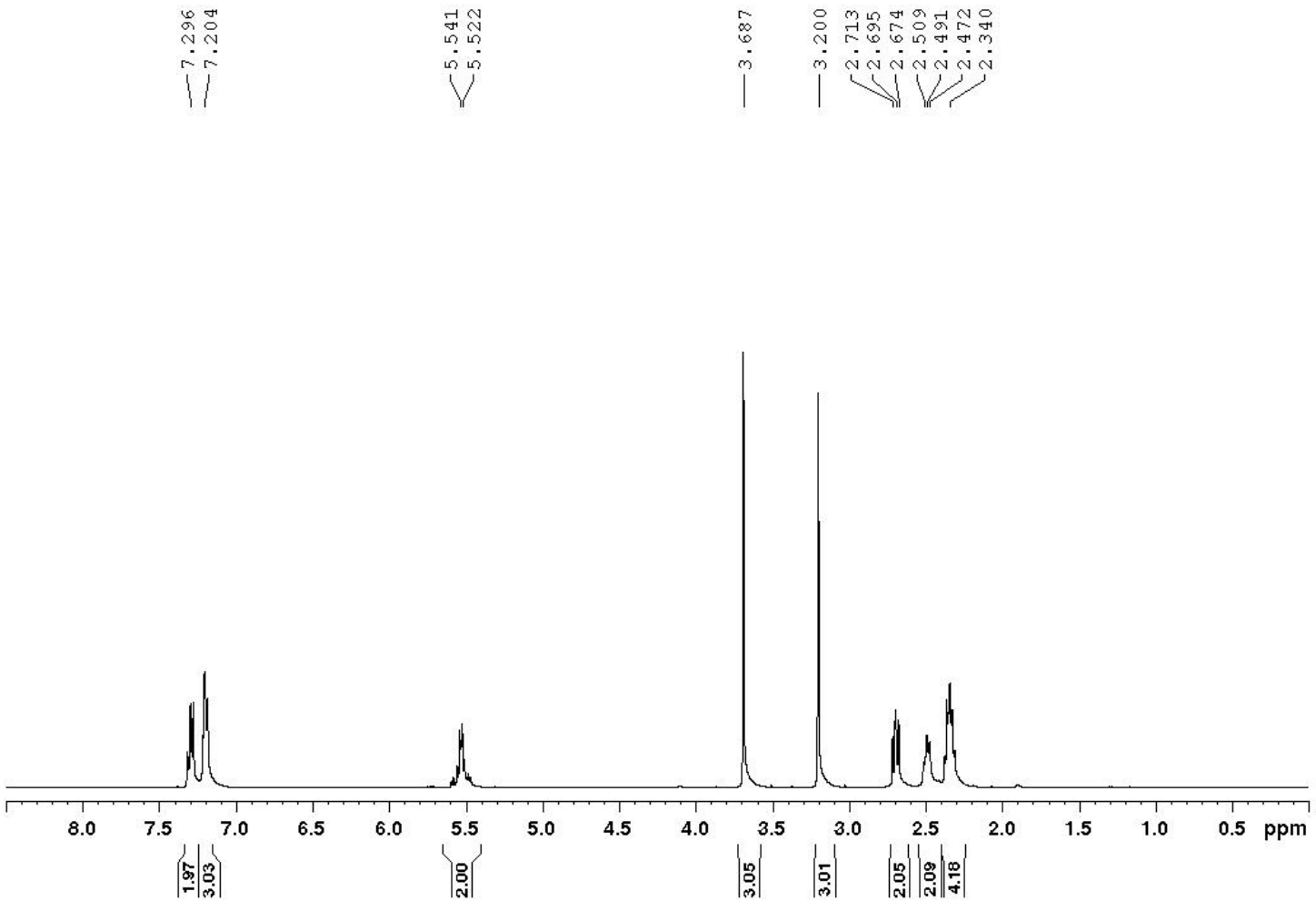


5b

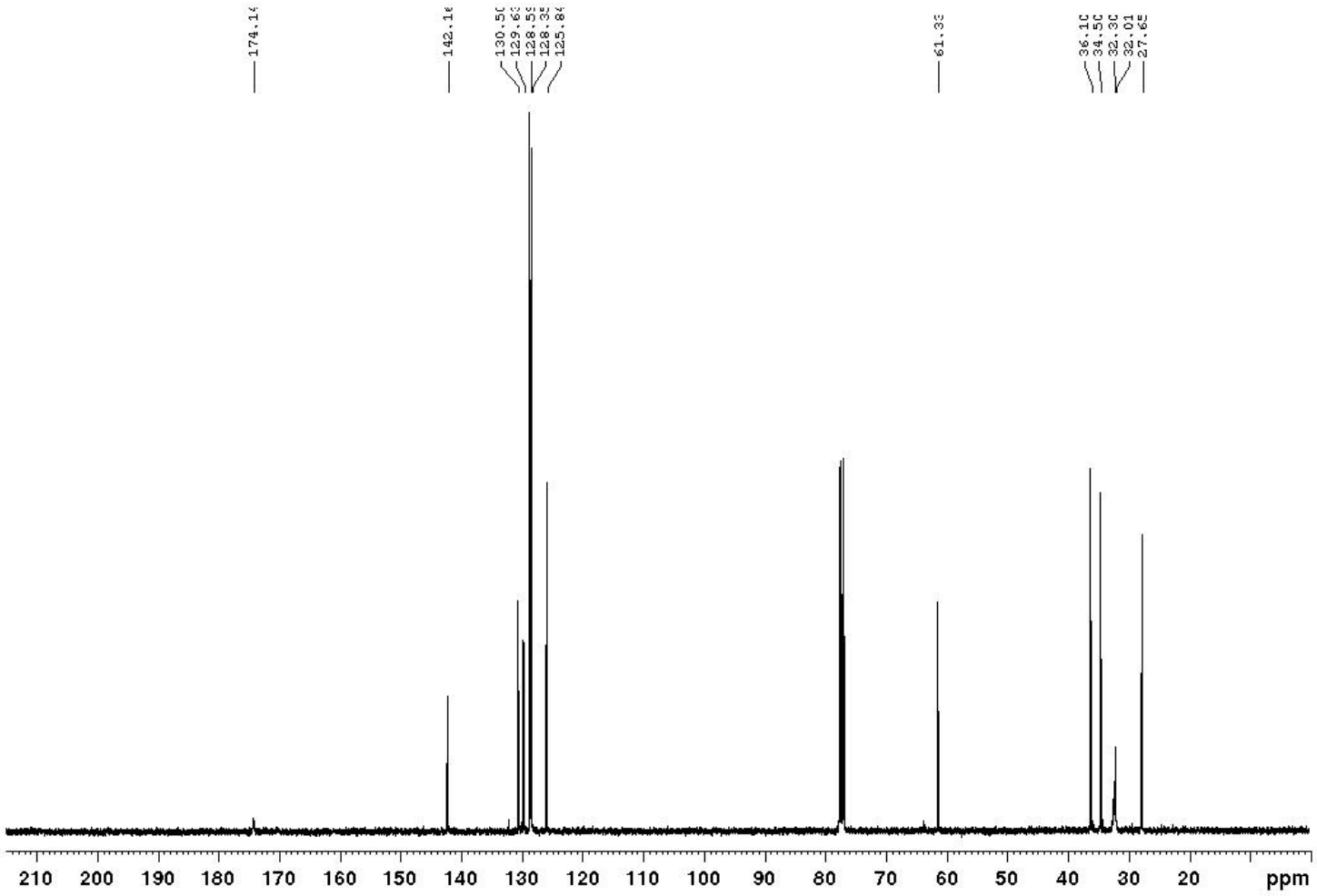


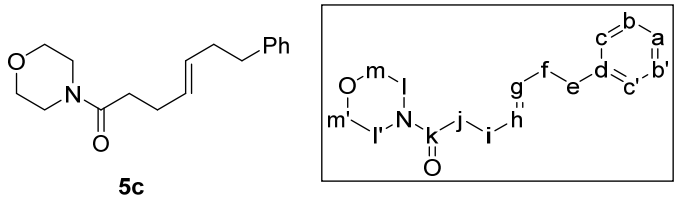
TLC analysis	R_f 0.5 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.35 (2H, m, b,b'), 7.15–7.25 (3H, m, a,c,c'), 5.45–5.65 (2H, m, g,h), 3.69 (3H, s, m), 3.20 (3H, s, l), 2.69 (2H, t, *J* = 7.4 Hz, e), 2.49 (2H, m, j), 2.20–2.40 (4H, m, f,i)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 174.14 (k), 142.16 (d), 130.50 (h), 129.63 (g), 128.59 (b,b'), 128.35 (c,c'), 125.84 (a), 61.33 (m), 36.10 (e), 34.50 (f), 32.30 (l), 32.01 (j), 27.65 (i)
IR (neat)	IR (neat) 2934 (C-H sp^3 stretch), 1661 (C=O stretch), 1452, 1413, 1383 (C-N stretch), 969, 698 cm^{-1}
HRMS (ESI)	$C_{15}H_{21}NNaO_2$ (M+Na): 270.1470, found 270.1469 *m/z*

^{1}H NMR of 5b


7.296
7.204
5.541
5.522
3.687
3.200
2.713
2.695
2.674
2.509
2.491
2.472
2.340
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.97
3.03
2.00
3.05
3.01
2.05
2.09
4.18

^{13}C NMR of 5b

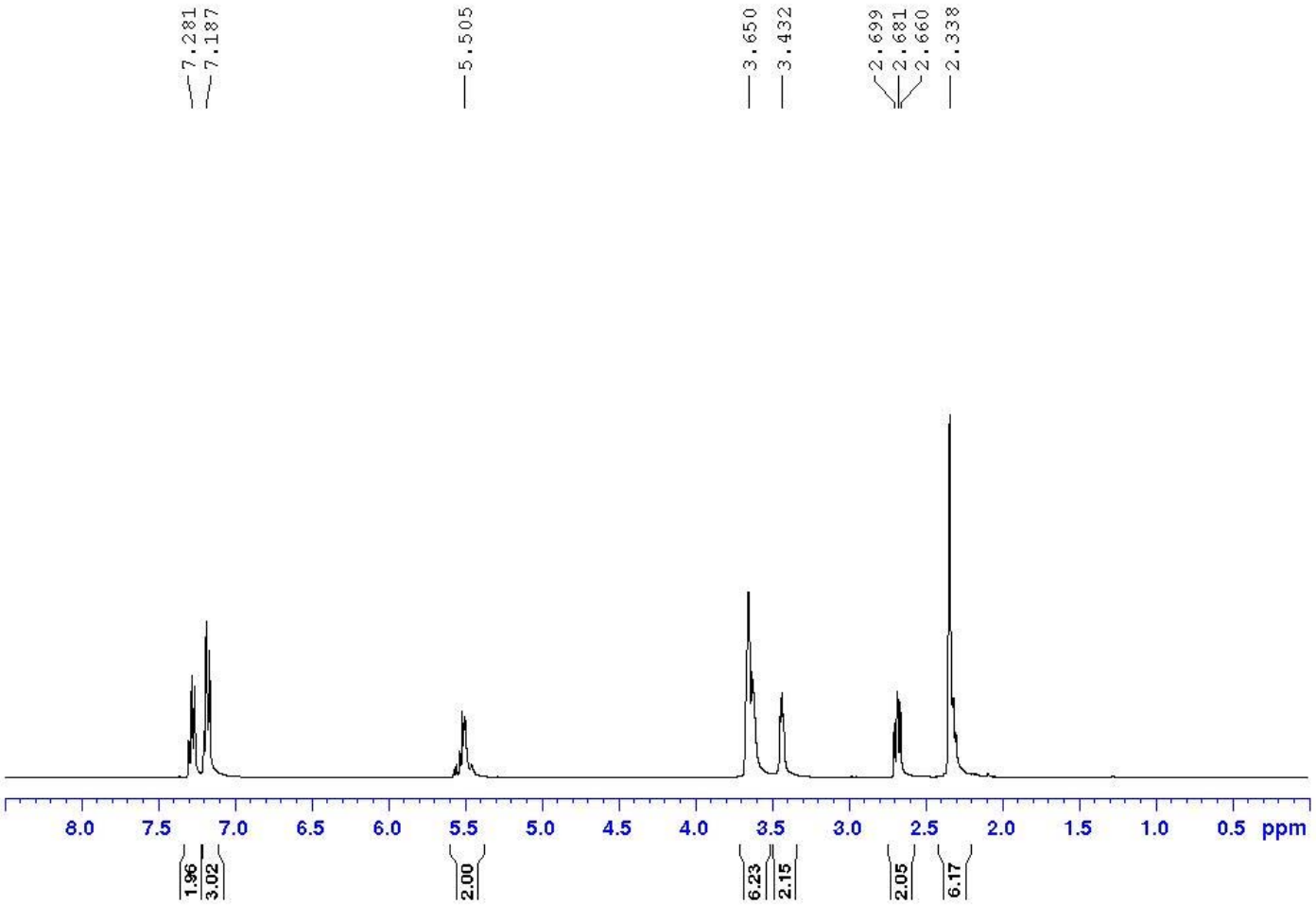

174.14
142.18
130.50
129.68
128.55
128.35
125.84
61.33
36.10
34.50
32.30
32.01
27.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



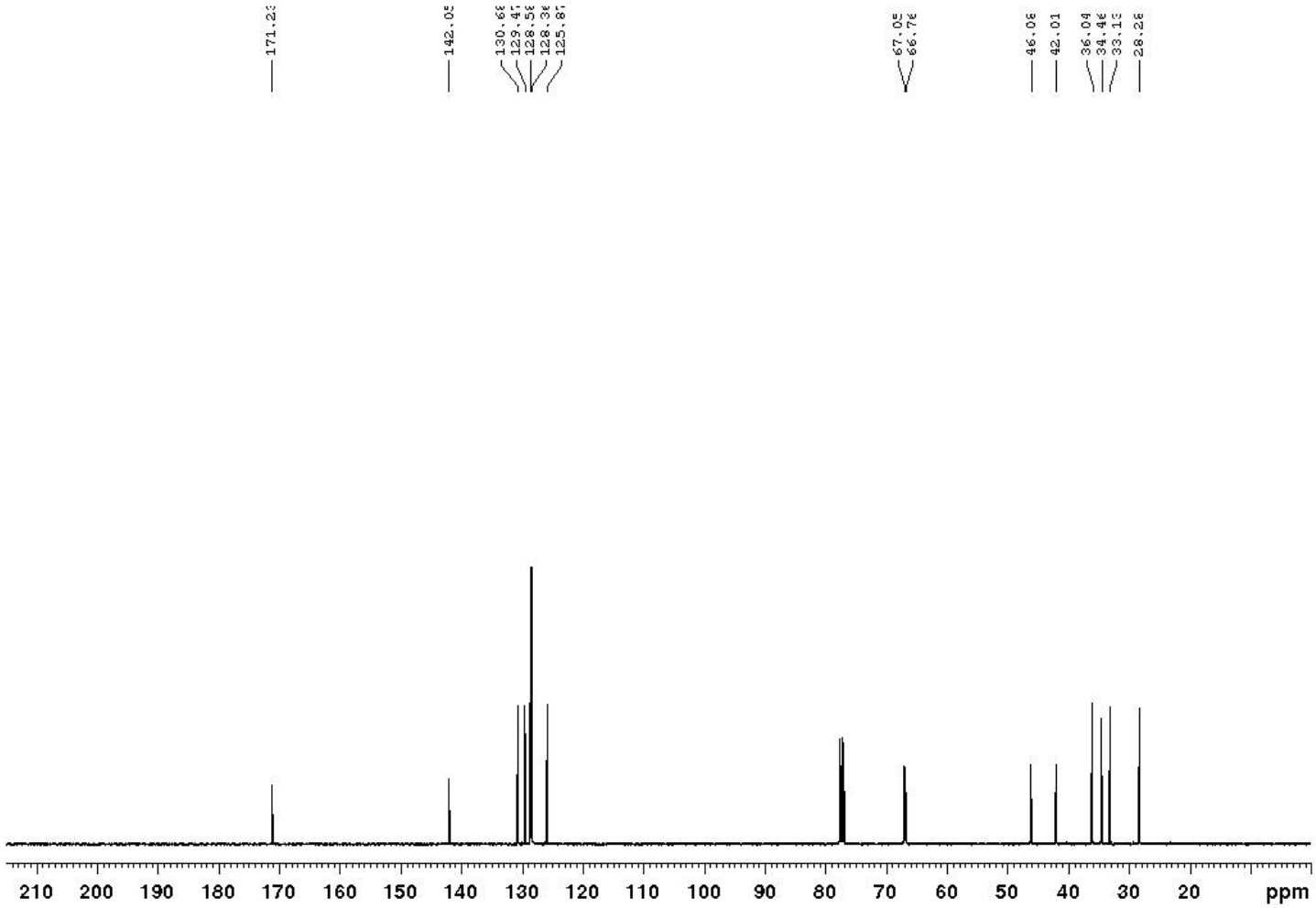
5c

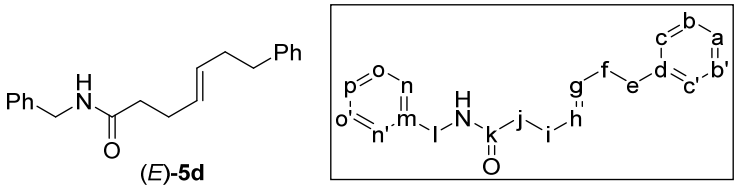
TLC analysis	R_f 0.4 (40:60 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.35 (2H, m, b,b'), 7.15–7.25 (3H, m, a,c,c'), 5.40–5.60 (2H, m, g,h), 3.55–3.70 (6H, m, l,l',m,m'), 3.35–3.50 (2H, m, l,l'), 2.68 (2H, t, *J* = 7.5 Hz, e), 2.20–2.40 (6H, m, f,i,j)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 171.23 (k), 142.05 (d), 131.68 (h), 129.47 (g), 128.59 (b,b'), 128.36 (c,c'), 125.87 (a), 67.05 and 66.76 (m,m'), 46.08 and 42.01 (l,l'), 36.04 (e), 34.46 (f), 33.13 (j), 28.28 (i)
IR (neat)	IR (neat) 2914 (C-H sp^3 stretch), 2852, 1642 (C=O stretch), 1428, 1113, 968, 699 cm^{-1}
HRMS (ESI)	$C_{17}H_{23}NNaO_2$ (M+Na): 296.1626, found 296.1628 *m/z*

^{1}H NMR of 5c


7.281
7.187
5.505
3.650
3.432
2.699
2.681
2.660
2.338
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.96
3.02
2.00
6.23
2.15
2.05
6.17

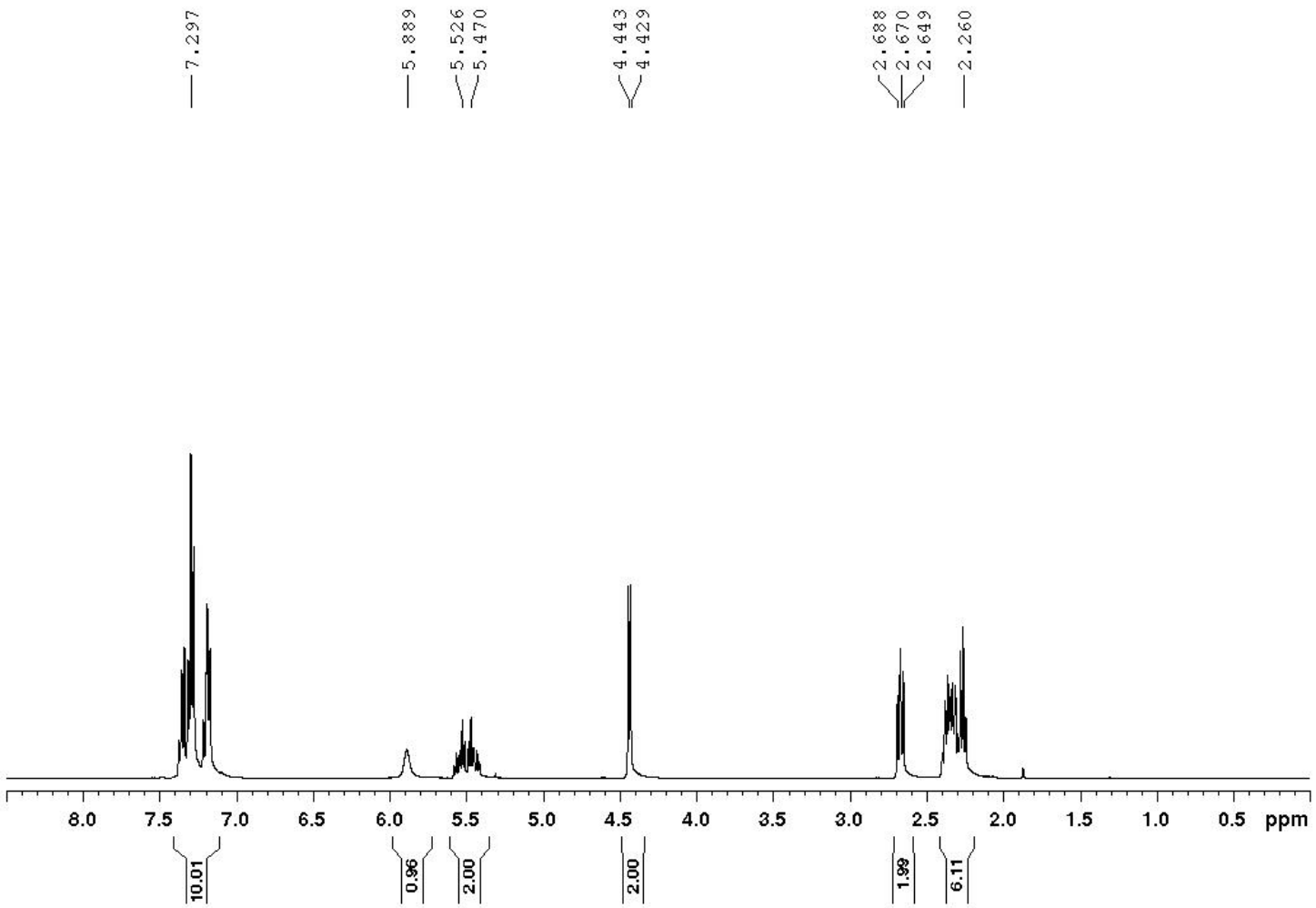
^{13}C NMR of 5c


171.2
142.0
130.6
129.4
128.5
128.3
125.8
67.0
66.7
46.0
42.0
36.0
34.4
33.1
28.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

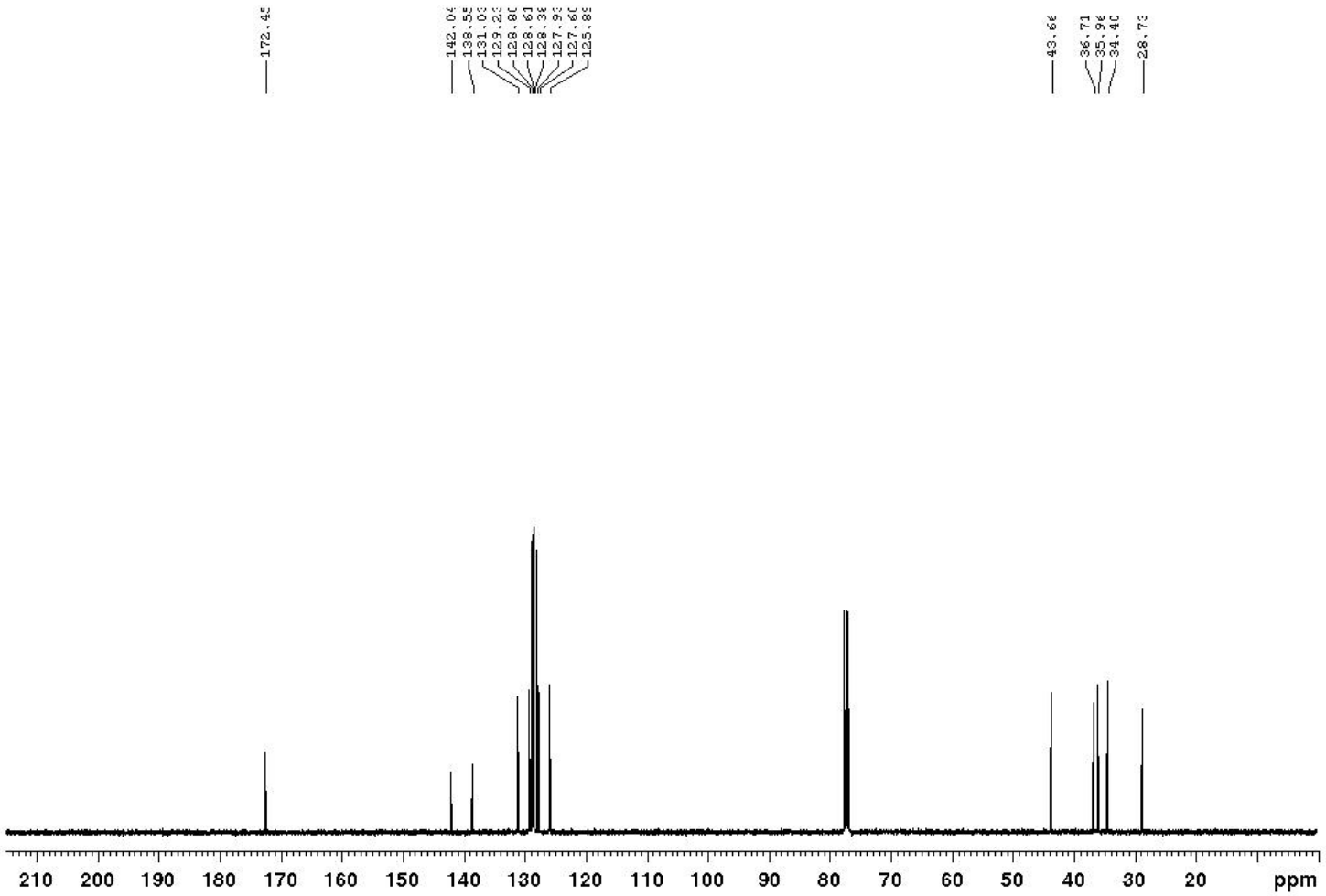


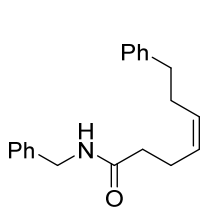
m.p.	65.5–66.5 ºC
TLC analysis	R_f 0.4 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.15–7.40 (10H, m, a,b,b',c,c',n,n',o,o',p), 5.89 (1H, br s, NH), 5.40–5.60 (2H, m, g,h), 4.44 (2H, d, *J* = 5.7 Hz, l), 2.67 (2H, t, *J* = 7.3 Hz, e), 2.20–2.40 (6H, m, f,i,j)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.45 (k), 142.04 (d), 138.55 (m), 131.03 (h), 129.23 (g), 128.80 (b,b'), 128.61 (o,o'), 128.38 (c,c'), 127.93 (n,n'), 127.60 (p), 125.89 (a), 43.66 (l), 36.71 (j), 35.96 (e), 34.40 (f), 28.73 (i)
IR (neat)	3285 (N-H stretch), 3028, 2915, 1635 (C=O stretch), 1537 (N-H bend), 1452, 1220, 965, 740, 694 cm^{-1}
HRMS (ESI)	$C_{20}H_{23}NNaO$ (M+Na): 316.1677, found 316.1681 *m/z*

^{1}H NMR of (*E*)-5d

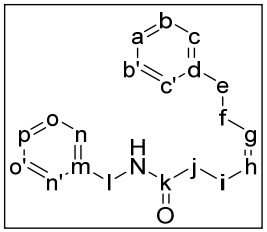

7.297
5.889
5.526
5.470
4.443
4.429
2.688
2.670
2.649
2.260
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
10.01
0.96
2.00
2.00
1.99
6.11

^{13}C NMR of (*E*)-5d



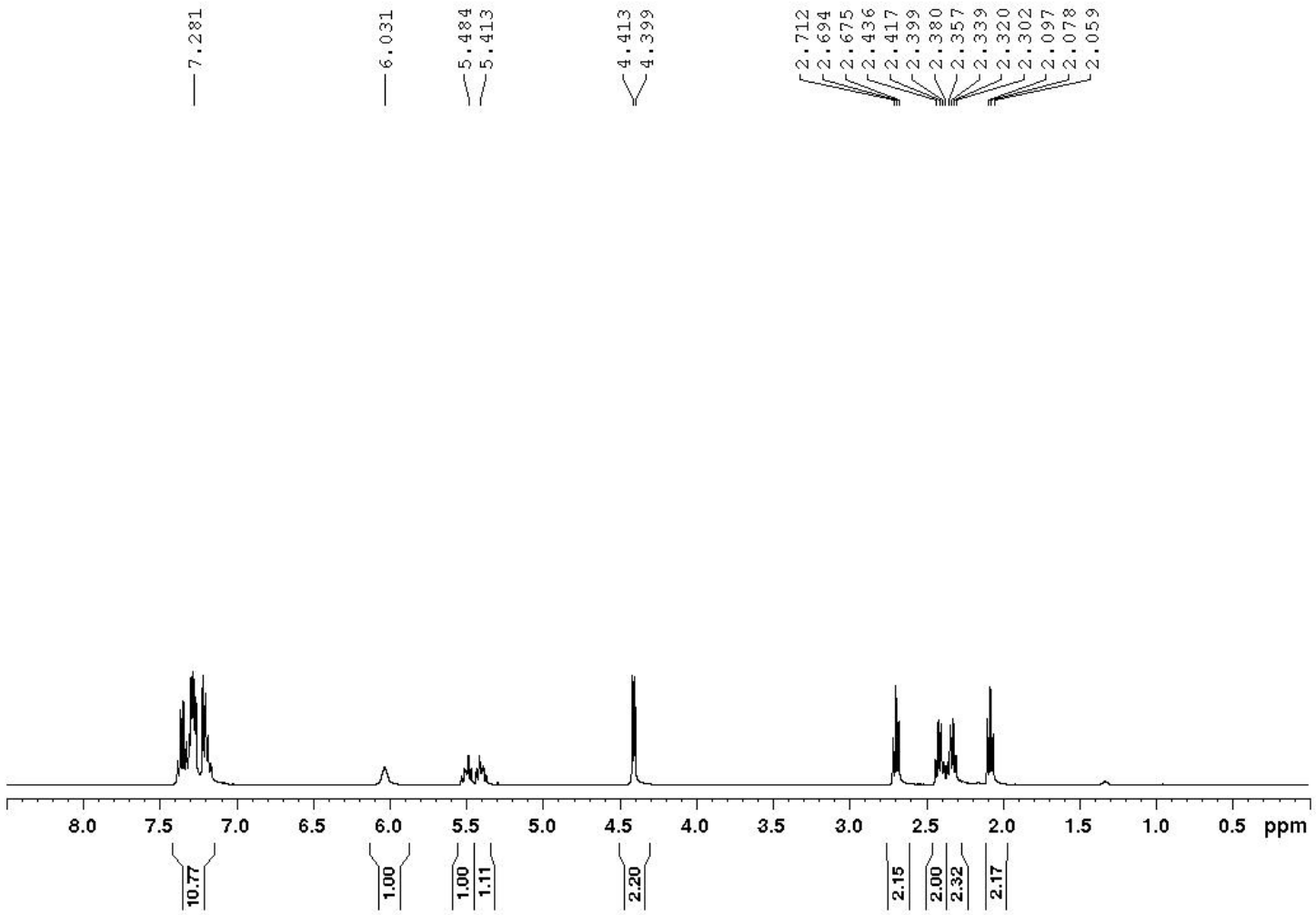


(*Z*)-**5d**

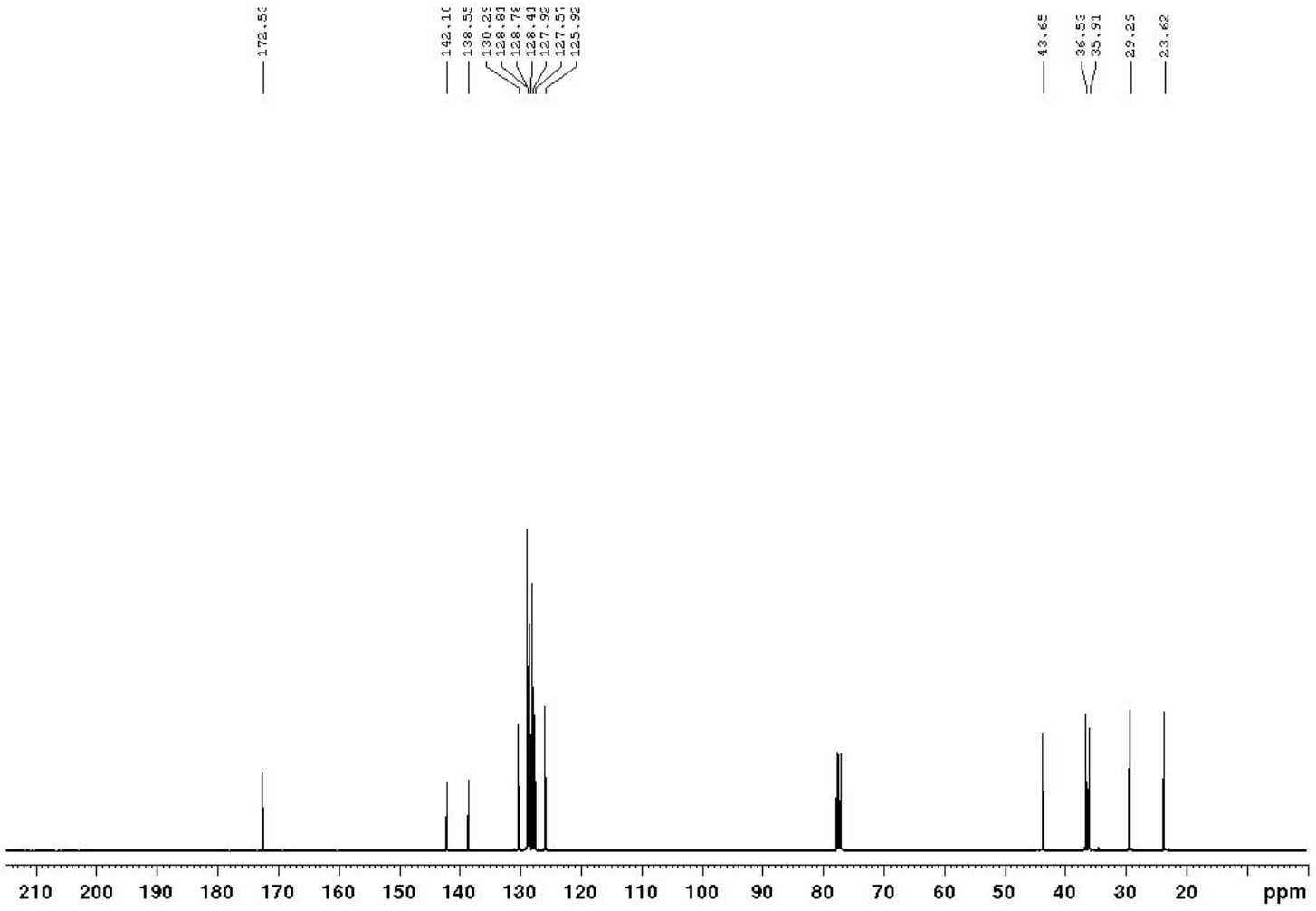


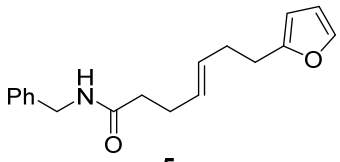
TLC analysis	R_f 0.4 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.15–7.40 (10H, m, a,b,b',c,c',n,n',o,o',p), 6.03 (1H, br s, NH), 5.45–5.55 (1H, m, h), 5.35–5.45 (1H, m, g), 4.41 (2H, d, *J* = 5.7 Hz, l), 2.69 (2H, t, *J* = 7.8 Hz, e), 2.41 (2H, q, *J* = 7.4 Hz, f), 2.33 (2H, q, *J* = 7.4 Hz, i), 2.08 (2H, t, *J* = 8.6 Hz, j)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.53 (k), 142.10 (d), 138.55 (m), 130.29 (h), 128.81 (b,b'), 128.78 (o,o'), 128.41 (g,c,c'), 127.92 (n,n'), 127.57 (p), 125.92 (a), 43.65 (l), 36.53 (j), 35.91 (e), 29.29 (f), 23.61 (i)
IR (neat)	3285 (N-H stretch), 3026, 2922, 1642 (C=O stretch), 1543 (N-H bend), 1495, 1453, 728, 695 cm^{-1}
HRMS (ESI)	$C_{20}H_{23}NNaO$ (M+Na): 316.1677, found 316.1681 *m/z*

^{1}H NMR of (*Z*)-5d

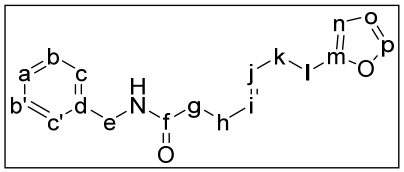

7.281
6.031
5.484
5.413
4.413
4.399
2.712
2.694
2.675
2.436
2.417
2.399
2.380
2.357
2.339
2.320
2.302
2.097
2.078
2.059
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
10.77
1.00
1.00
1.11
2.20
2.15
2.00
2.32
2.17

^{13}C NMR of (*Z*)-5d



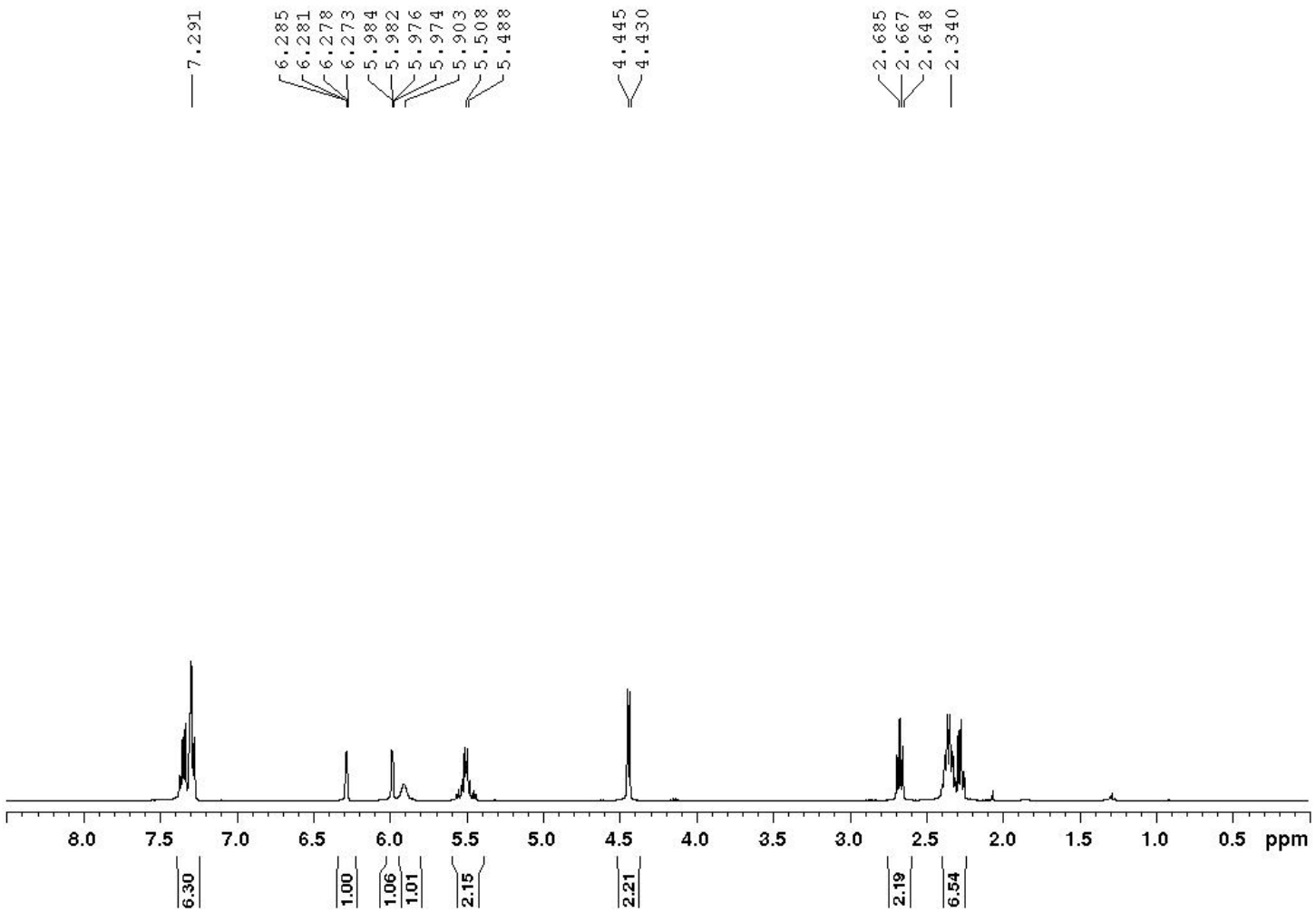


5e

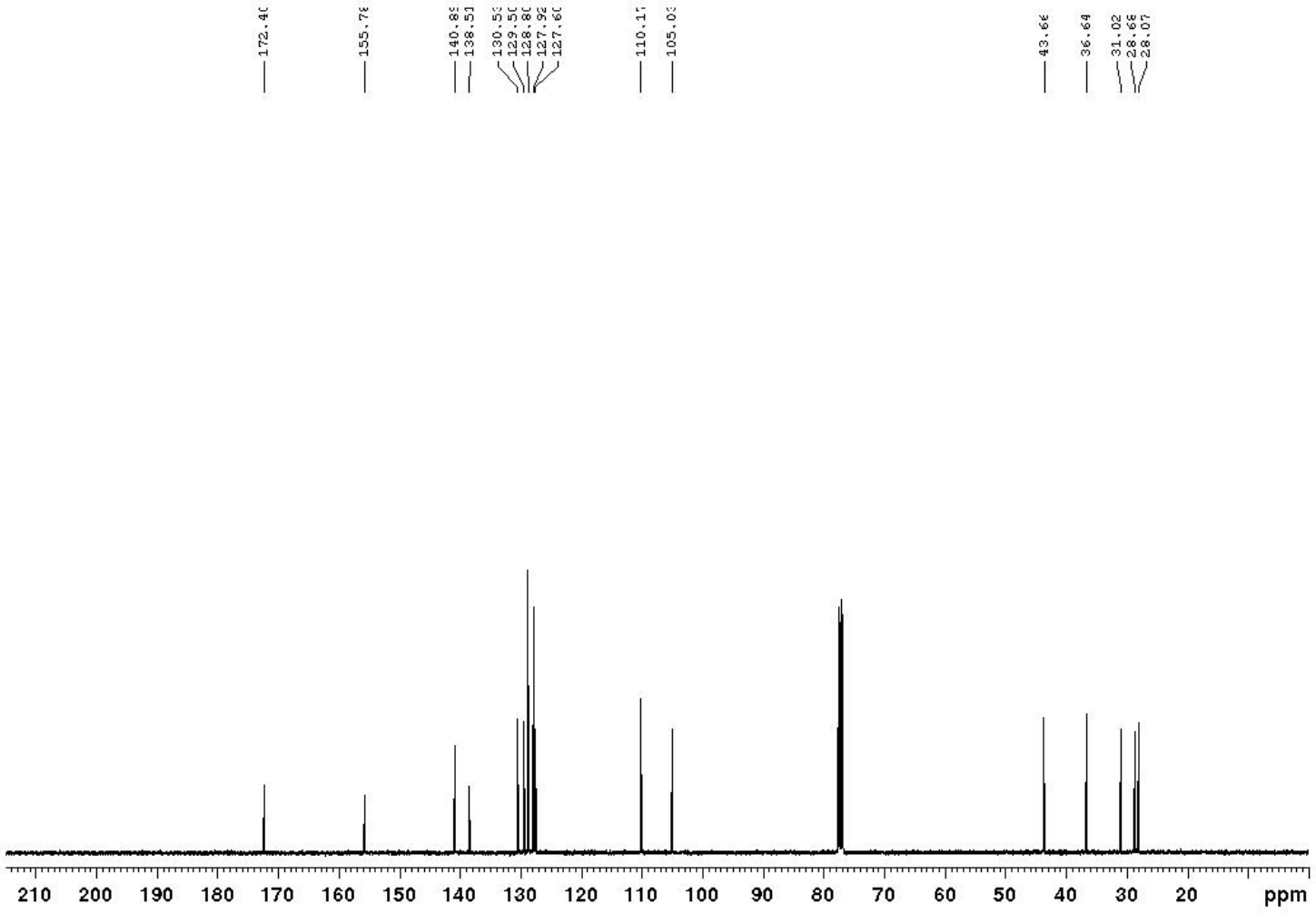


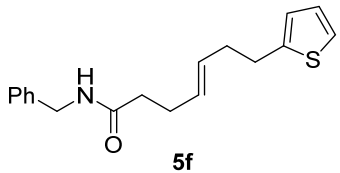
m.p.	60.5–61.5 ºC
TLC analysis	R_f 0.35 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.40 (6H, m, a,b,b',c,c',p), 6.28 (1H, dd, *J* = 3.0 Hz, 1.9 Hz, o), 5.98 (1H, dd, *J* = 3.1 Hz, 0.6 Hz, n), 5.90 (1H, br s, NH), 5.40–5.60 (2H, m, i,j), 4.44 (2H, d, *J* = 5.7 Hz, e), 2.67 (2H, t, *J* = 7.4 Hz, l), 2.20–2.40 (6H, m, g,h,k)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.40 (f), 155.78 (m), 140.89 (p), 138.51 (d), 130.53 (i), 129.50 (j), 128.80 (b,b'), 127.92 (c,c'), 127.60 (a), 110.17 (o), 105.03 (n), 43.66 (e), 36.64 (g), 31.02 (k), 28.68 (h), 28.07 (l)
IR (neat)	3293 (N-H stretch), 2916, 1632 (C=O stretch), 1538 (N-H bend), 1506, 1453, 729, 695 cm^{-1}
HRMS (ESI)	$C_{18}H_{21}NNaO_2$ (M+Na): 306.1470, found 306.1477 *m/z*

^{1}H NMR of 5e

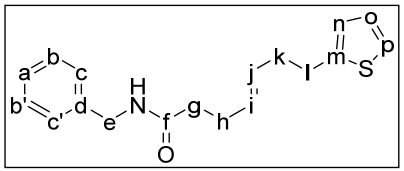

7.291
6.285
6.281
6.278
6.273
5.984
5.982
5.976
5.974
5.903
5.508
5.488
4.445
4.430
2.685
2.667
2.648
2.340
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
6.30
1.00
1.06
1.01
2.15
2.21
2.19
6.54

^{13}C NMR of 5e


172.40
155.78
140.85
138.51
130.53
129.50
128.80
127.92
127.60
110.17
105.03
43.66
36.64
31.02
28.68
28.07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

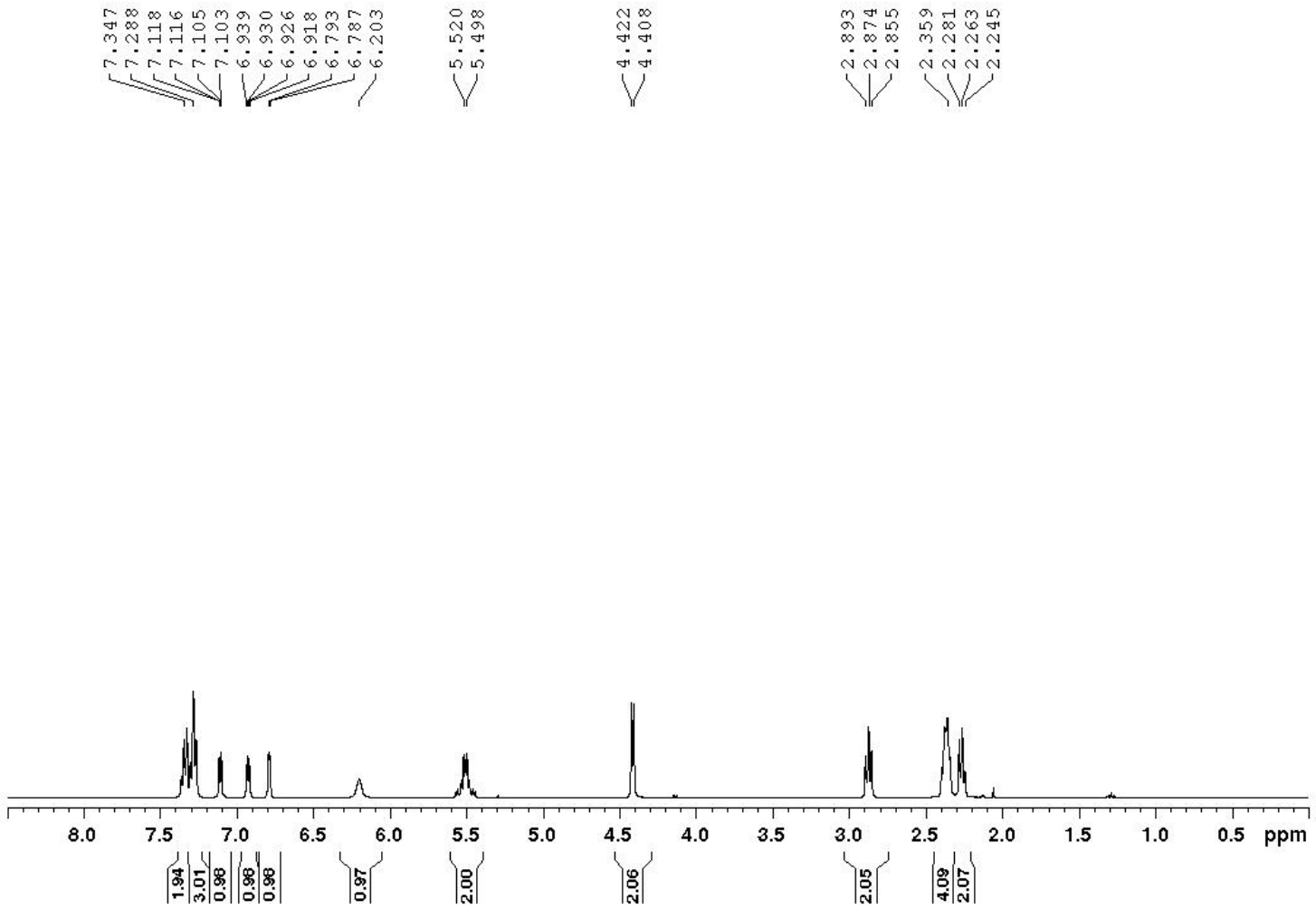


5f

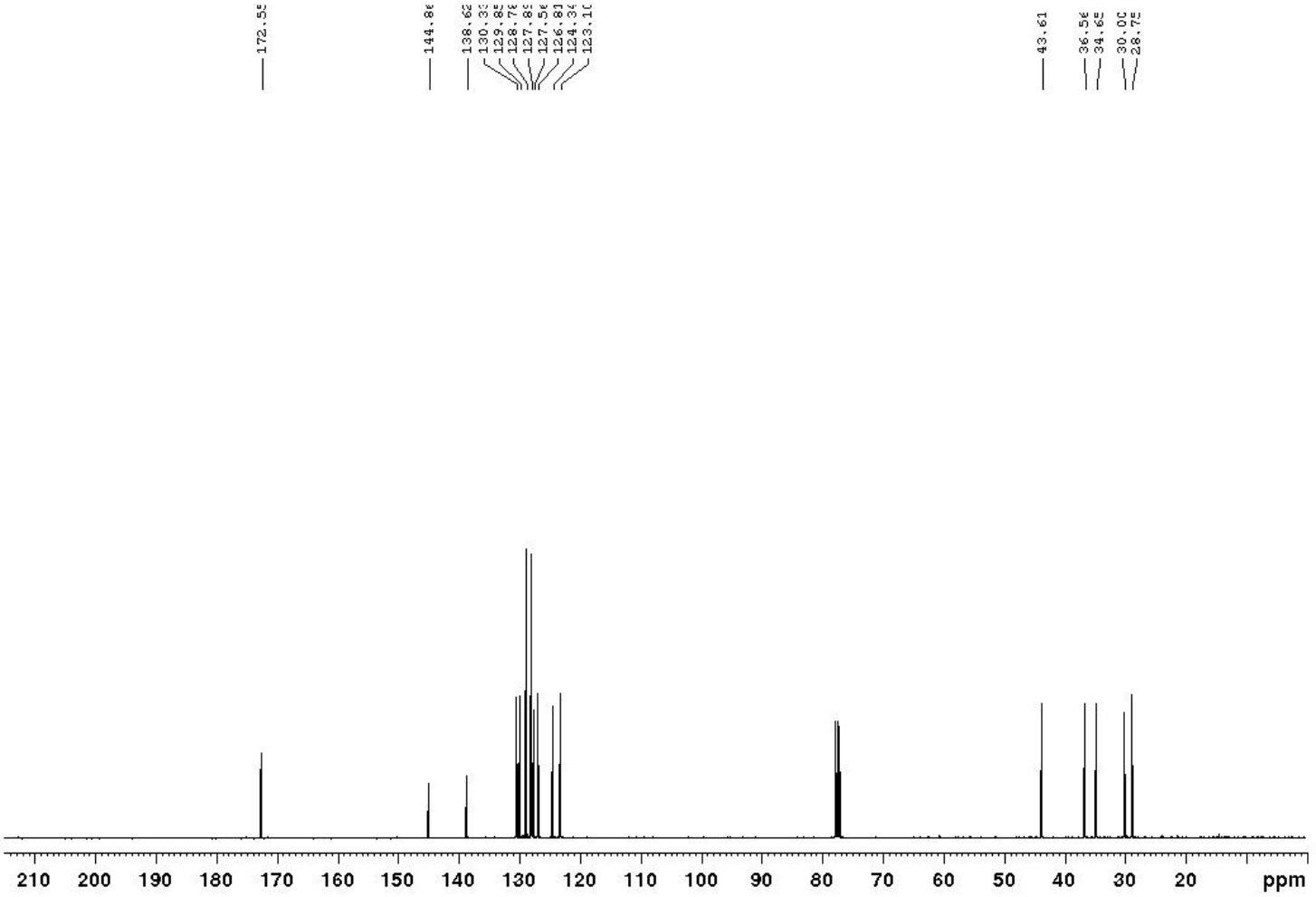


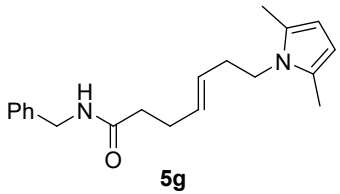
m.p.	62.0–63.0 ºC
TLC analysis	R_f 0.35 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.40 (2H, m, b,b'), 7.25–7.30 (3H, m, a, c,c'), 7.12 (1H, dd, *J* = 5.2 Hz, 0.8 Hz, p), 6.93 (1H, dd, *J* = 4.9 Hz, 3.5 Hz, o), 6.79 (1H, d, *J* = 2.6 Hz, n), 6.20 (1H, br s, NH), 5.40–5.60 (2H, m, i,j), 4.42 (2H, d, *J* = 5.7 Hz, e), 2.87 (2H, t, *J* = 7.4 Hz, l), 2.30–2.40 (4H, m, h,k), 2.26 (2H, t, *J* = 7.1 Hz, g)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.55 (f), 144.86 (m), 138.62 (d), 130.32 (i), 129.85 (j), 128.78 (b,b'), 127.89 (c,c'), 127.56 (a), 126.81 (o), 124.34 (p), 123.10 (n), 43.61 (e), 36.56 (g), 34.65 (k), 30.00 (h), 28.75 (l)
IR (neat)	3291 (N-H stretch), 3030, 2915, 1629 (C=O stretch), 1531 (N-H bend), 1453, 968, 746, 693 cm^{-1}
HRMS (ESI)	$C_{18}H_{21}NNaOS$ (M+Na): 322.1242, found 322.1243 *m/z*

^{1}H NMR of 5f

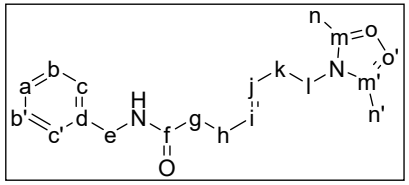

7.347
7.288
7.118
7.116
7.105
7.103
6.939
6.930
6.926
6.918
6.793
6.787
6.203
5.520
5.498
4.422
4.408
2.893
2.874
2.855
2.359
2.281
2.263
2.245
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.94
3.01
0.98
0.98
0.98
0.97
2.00
2.06
2.05
4.09
2.07

^{13}C NMR of 5f


172.55
144.88
138.62
130.33
129.85
128.71
127.85
127.58
126.81
124.34
123.10
43.61
36.56
34.65
30.00
28.72
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

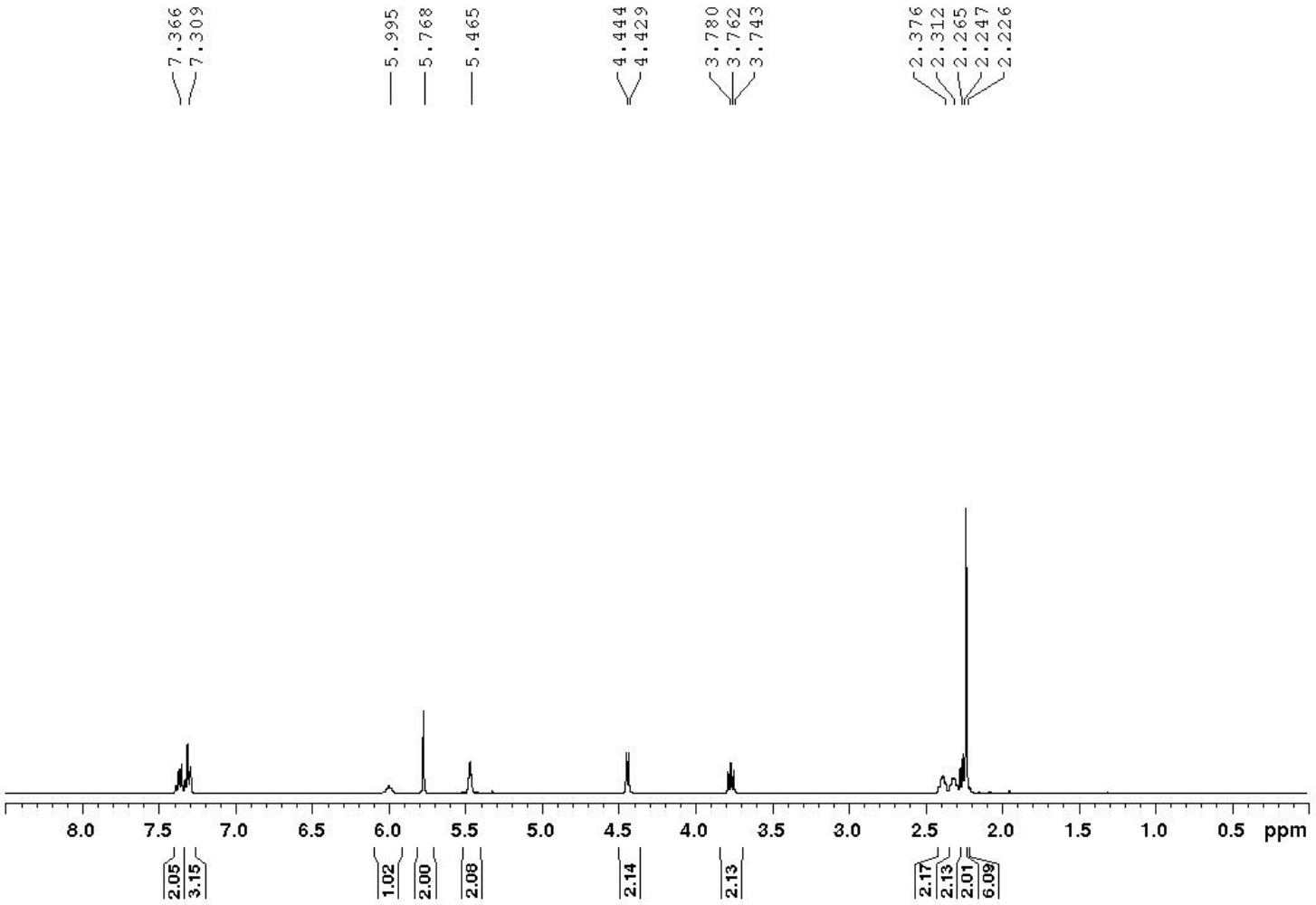


5g

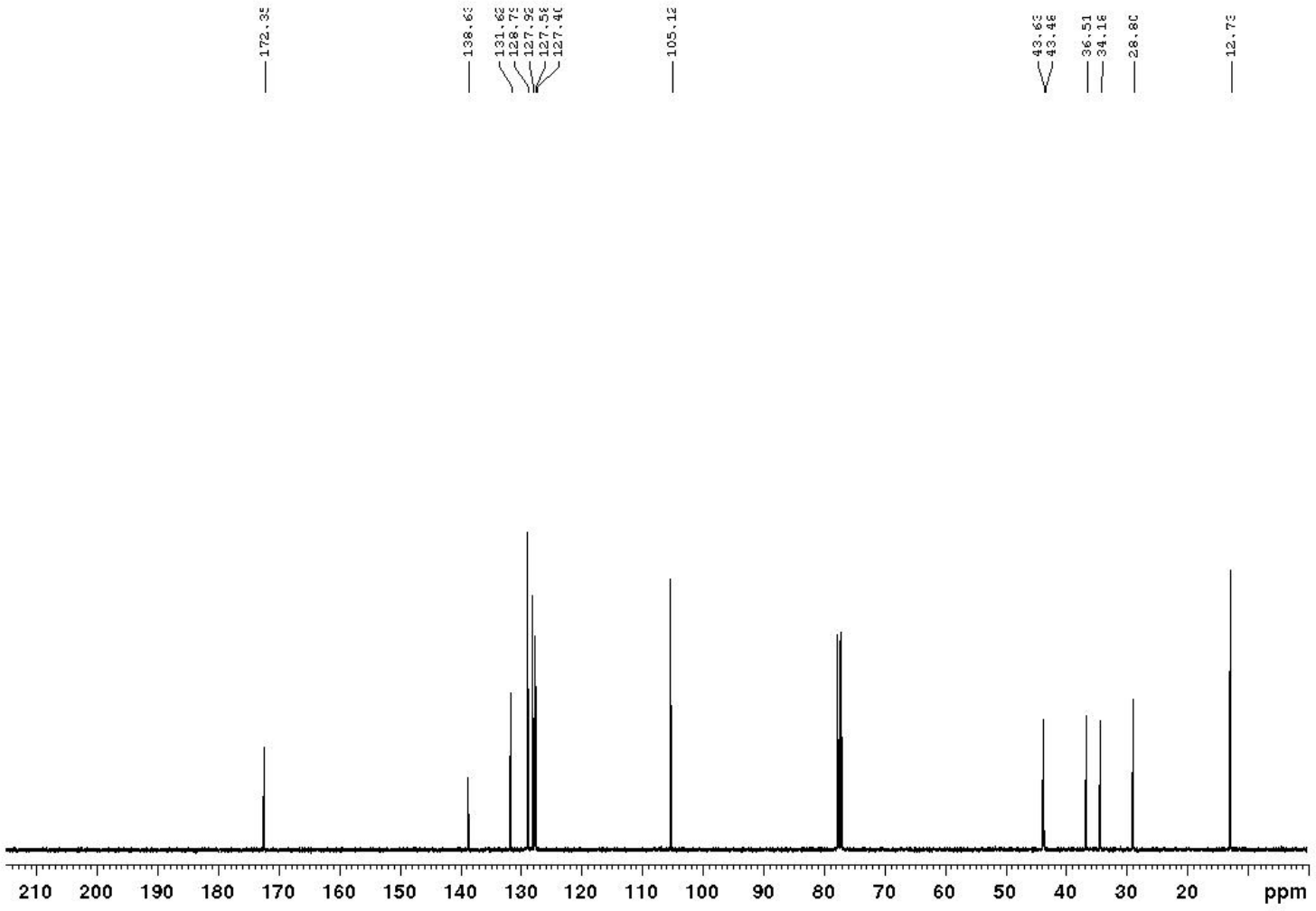


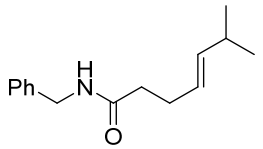
TLC analysis	R_f 0.5 (40:60 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.35–7.40 (2H, m, b,b'), 7.25–7.35 (3H, m, a,c,c'), 5.99 (1H, br s, NH), 5.77 (2H, s, o,o'), 5.40–5.50 (2H, m, i,j), 4.44 (2H, d, *J* = 5.8 Hz, e), 3.76 (2H, t, *J* = 7.4 Hz, l), 2.35–2.45 (2H, m, h), 2.25–2.35 (2H, m, k), 2.25 (2H, t, *J* = 7.0 Hz, g, *overlapping with* n,n'), 2.23 (6H, s, n,n')
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.35 (f), 138.63 (d), 131.62 (i), 128.79 (b,b',m,m'), 127.92 (c,c'), 127.58 (a), 127.40 (j), 105.12 (o,o'), 43.63 (e), 43.48 (l), 36.51 (g), 34.18 (k), 28.80 (h), 12.73 (n,n')
IR (neat)	3283 (N-H stretch), 2914, 1643 (C=O stretch), 1539 (N-H bend), 1453, 1407, 970, 743, 697 cm^{-1}
HRMS (ESI)	$C_{20}H_{26}N_2NaO$ (M+Na): 333.1943, found 333.1950 *m/z*

^{1}H NMR of 5g

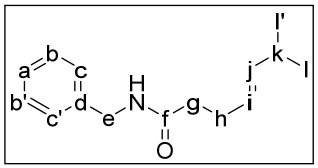

7.366
7.309
5.995
5.768
5.465
4.444
4.429
3.780
3.762
3.743
2.376
2.312
2.265
2.247
2.226
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.05
3.15
1.02
2.00
2.08
2.14
2.13
2.17
2.13
2.01
6.09

^{13}C NMR of 5g


172.35
138.63
131.66
128.75
127.92
127.58
127.40
105.12
43.63
43.48
36.51
34.18
28.80
12.73
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

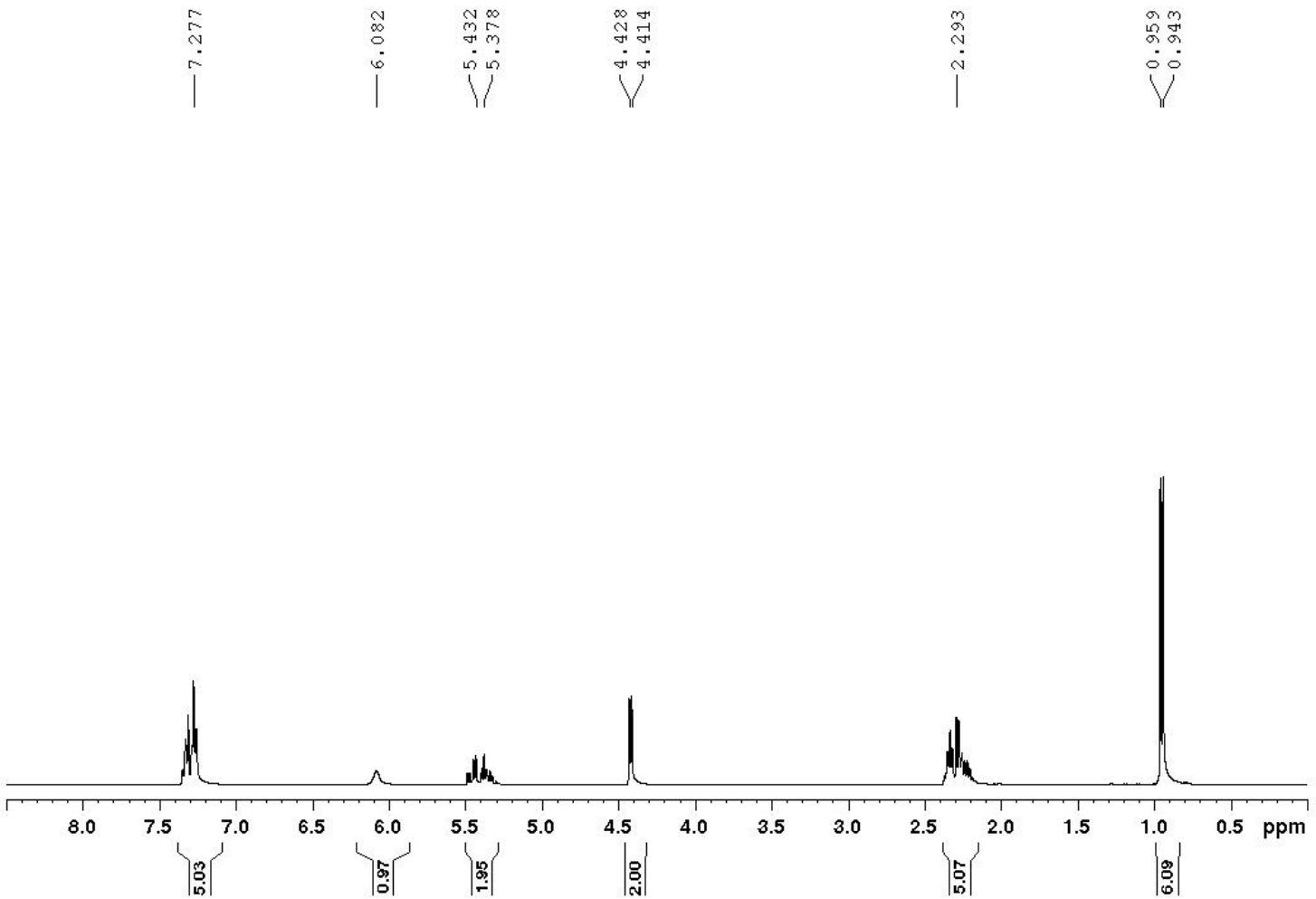


5h

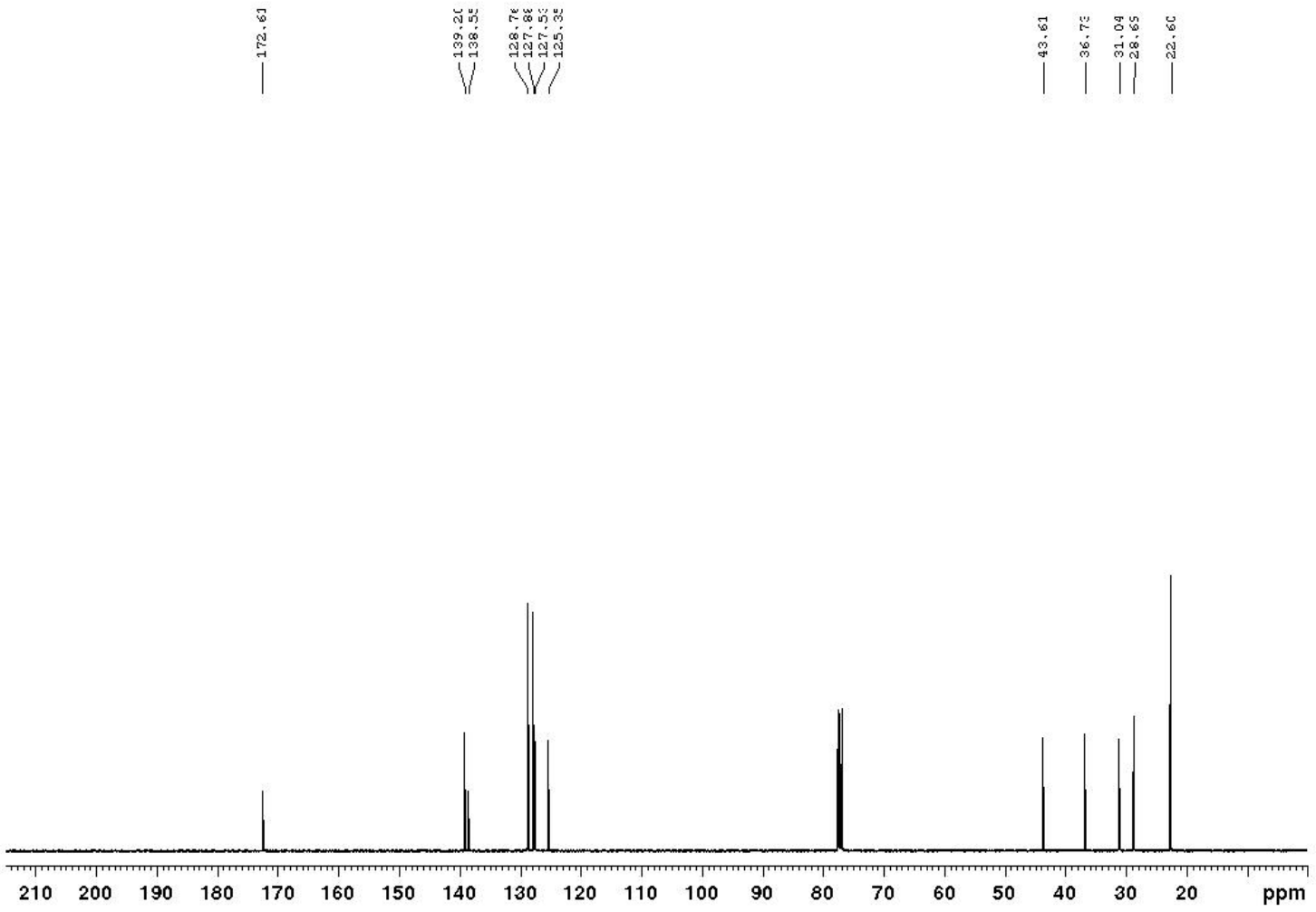


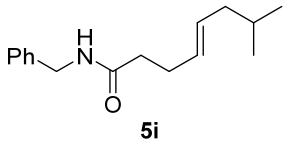
m.p.	45.0–45.5 ºC
TLC analysis	R_f 0.4 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.15–7.40 (5H, m, a,b,b',c,c'), 6.08 (1H, br s, NH), 5.30–5.50 (2H, m, i,j), 4.42 (2H, d, *J* = 5.7 Hz, e), 2.15–2.40 (5H, m, g,h,k), 0.95 (6H, d, *J* = 6.7 Hz, l,l')
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.61 (f), 139.20 (d), 138.55 (j), 128.76 (b,b'), 127.88 (c,c'), 127.53 (i), 125.35 (a), 43.61 (e), 36.73 (g), 31.04 (k), 28.69 (h), 22.60 (l,l')
IR (neat)	3292 (N-H stretch), 2959, 2928, 2870, 1633 (C=O stretch), 1534 (N-H bend), 1454, 1407, 968, 746, 694 cm^{-1}
HRMS (ESI)	$C_{15}H_{21}NNaO$ (M+Na): 254.1521, found 254.1526 *m/z*

^{1}H NMR of 5h

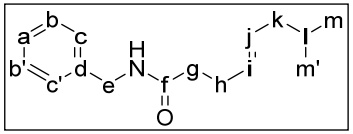

7.277
6.082
5.432
5.378
4.428
4.414
2.293
0.959
0.943
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.03
0.97
1.95
2.00
5.07
6.09

^{13}C NMR of 5h


172.61
139.20
138.55
128.76
127.88
127.53
125.35
43.61
36.75
31.04
28.65
22.60
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

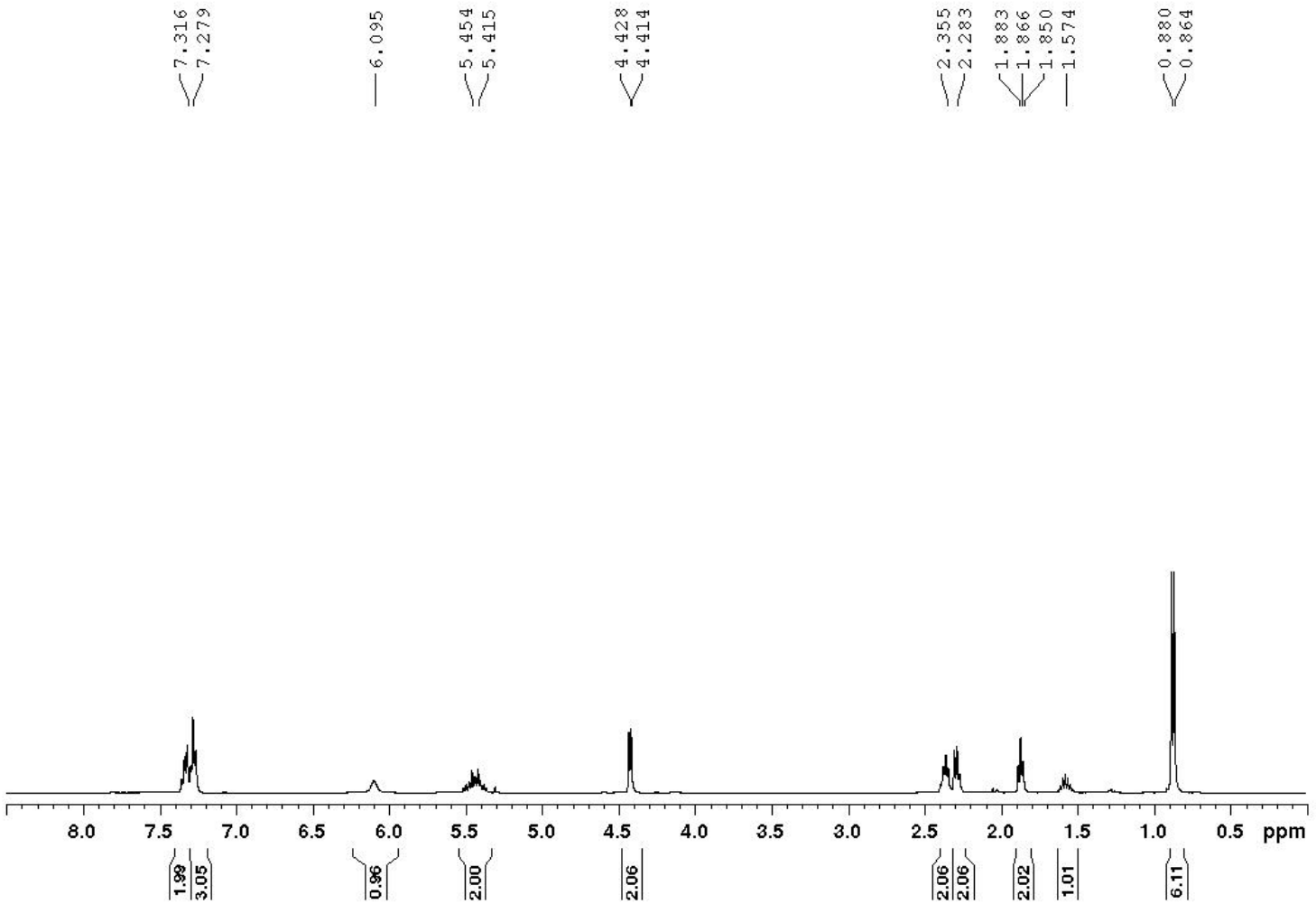


5i

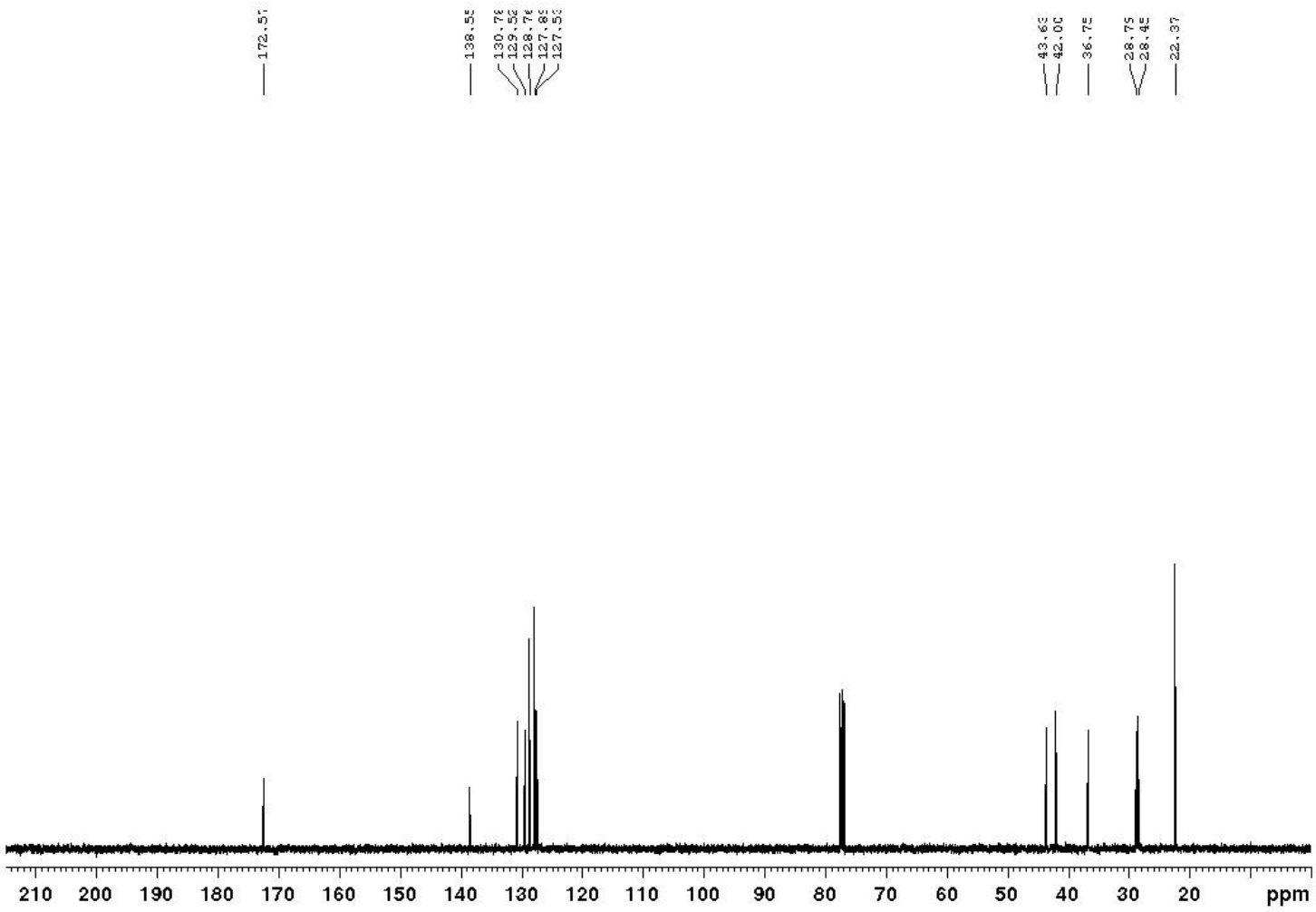


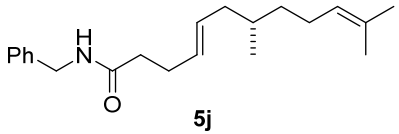
TLC analysis	R_f 0.4 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.40 (2H, m, b,b'), 7.20–7.30 (3H, m, a,c,c'), 6.09 (1H, br s, NH), 5.35–5.55 (2H, m, i,j), 4.42 (2H, d, *J* = 5.6 Hz, e), 2.30–2.40 (2H, m, h), 2.25–2.30 (2H, m, g) 1.87 (2H, t, *J* = 6.6 Hz, k), 1.50–1.65 (1H, m, l), 0.87 (6H, d, *J* = 6.6 Hz, m,m')
^{13}C NMR (100 MHz, $CDCl_3$)	172.57 (f), 138.55 (d), 130.78 (i), 129.52 (j), 128.76 (b,b'), 127.89 (c,c'), 127.53 (a), 43.63 (e), 42.00 (k), 36.75 (g), 28.79 (h), 28.45 (l), 22.37 (m,m')
IR (neat)	3286 (N-H stretch), 2953, 2923, 2868, 1642 (C=O stretch), 1544 (N-H bend), 1454, 967, 696 cm^{-1}
HRMS (ESI)	$C_{16}H_{23}NNaO$ (M+Na): 268.1677, found 268.1689 *m/z*

^{1}H NMR of 5i

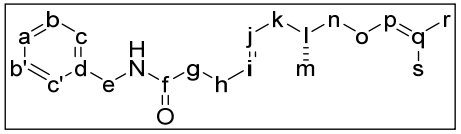

7.316
7.279
6.095
5.454
5.415
4.428
4.414
2.355
2.283
1.883
1.866
1.850
1.574
0.880
0.864
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.99
3.05
0.96
2.00
2.06
2.06
2.06
2.02
1.01
6.11

^{13}C NMR of 5i


172.57
138.55
130.78
129.52
128.78
127.85
127.53
43.63
42.00
36.75
28.75
28.45
22.37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

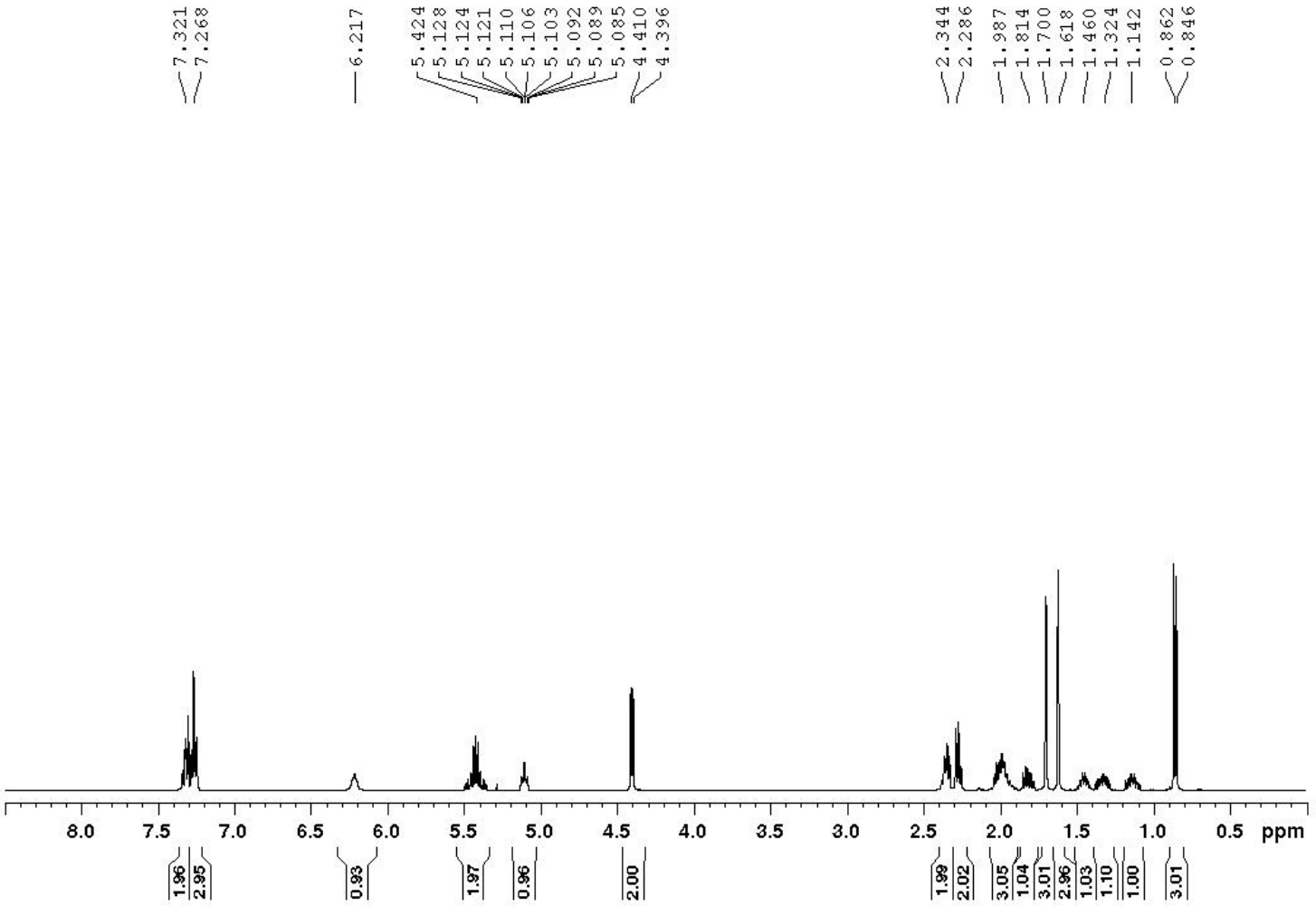


5j



$[\alpha]_D^{20}$	+6.2° (*c* 2.0, $CHCl_3$)
TLC analysis	R_f 0.4 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.35 (2H, m, b,b'), 7.25–7.30 (3H, m, a,c,c'), 6.22 (1H, br s, NH), 5.35–5.50 (2H, m, i,j), 5.11 (1H, tt, *J* = 7.2 Hz, 1.3 Hz, p), 4.40 (2H, d, *J* = 5.8 Hz, e), 2.30–2.40 (2H, m, h), 2.25–2.30 (2H, m, g), 1.90–2.05 (3H, m, k,o), 1.75–1.85 (1H, m, k), 1.70 (3H, s, r), 1.62 (3H, s, s),1.40–1.50 (1H, m, l), 1.25–1.40 (1H, m, n), 1.10–1.20 (1H, m, n), 0.86 (3H, d, *J* = 6.6 Hz, m)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.62 (f), 138.58 (d), 131.17 (q), 130.47 (i), 129.69 (j), 128.73 (xwinb,b'), 127.86 (c,c'), 127.49 (a), 124.98 (p), 43.60 (e), 40.05 (k), 36.77 (n), 36.71 (g), 32.77 (l), 28.83 (h), 25.85 (r), 25.70 (o), 19.46 (m), 17.77 (s)
IR (neat)	3277 (N-H stretch), 2959, 2911, 1643 (C=O stretch), 1545 (N-H bend), 1453, 968, 696 cm^{-1}
HRMS (ESI)	$C_{21}H_{31}NNaO$ (M+Na): 336.2303, found 336.2316 *m/z*

^{1}H NMR of 5j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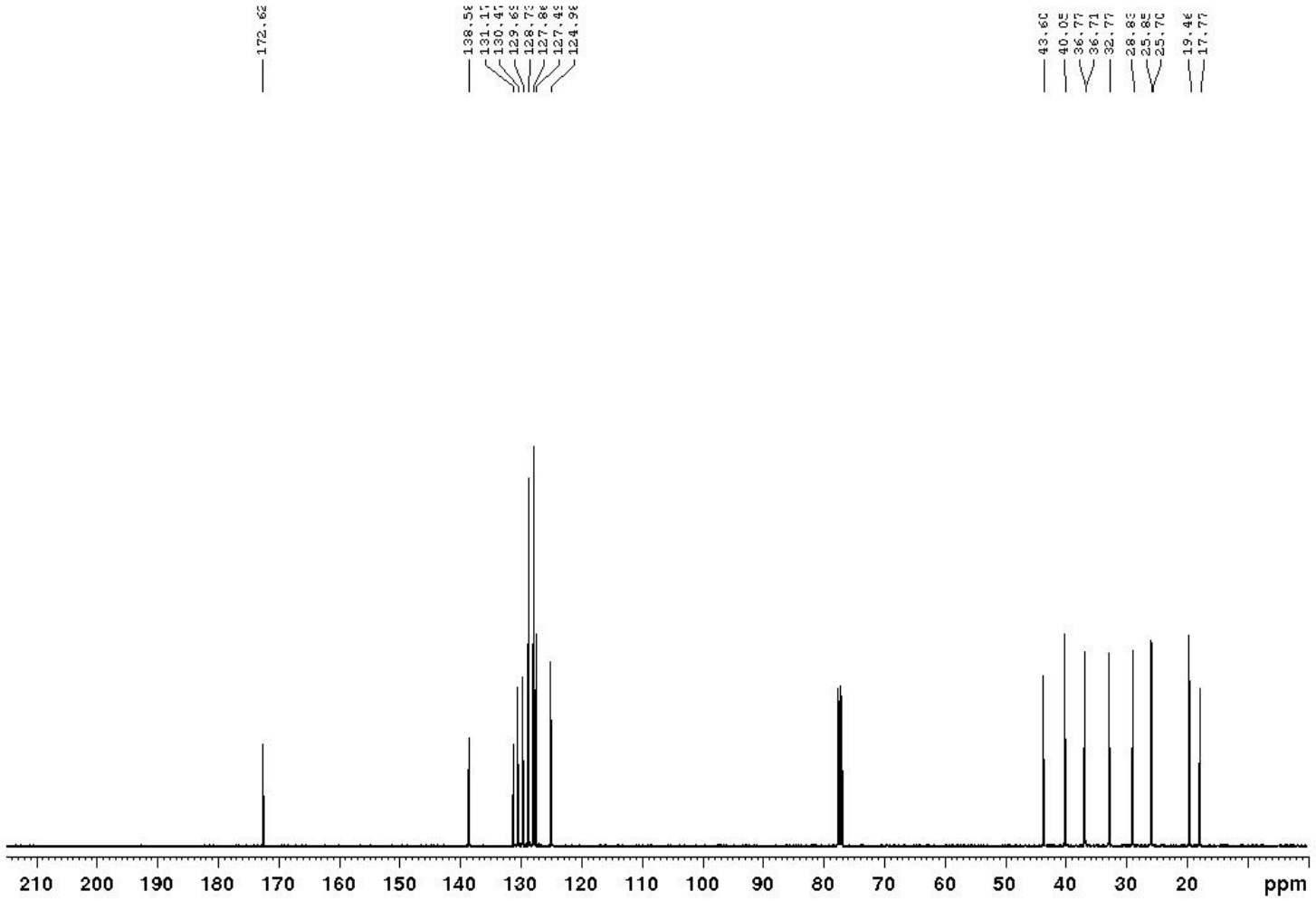
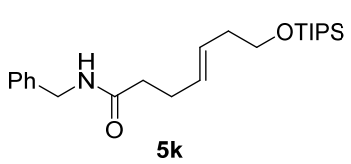
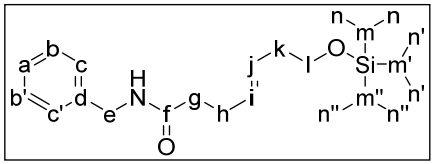
7.268
6.217
5.424
5.128
5.124
5.121
5.110
5.106
5.103
5.092
5.089
5.085
4.410
4.396
2.344
2.286
1.987
1.814
1.700
1.618
1.460
1.324
1.142
0.862
0.846
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.96
2.95
0.93
1.97
0.96
2.00
1.99
2.02
3.05
1.04
3.01
2.96
1.03
1.10
1.00
3.01

^{13}C NMR of 5j


172.62
138.58
131.17
130.47
129.65
128.73
127.88
127.49
124.98
43.60
40.05
36.77
36.71
32.77
28.83
25.85
25.70
19.46
17.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

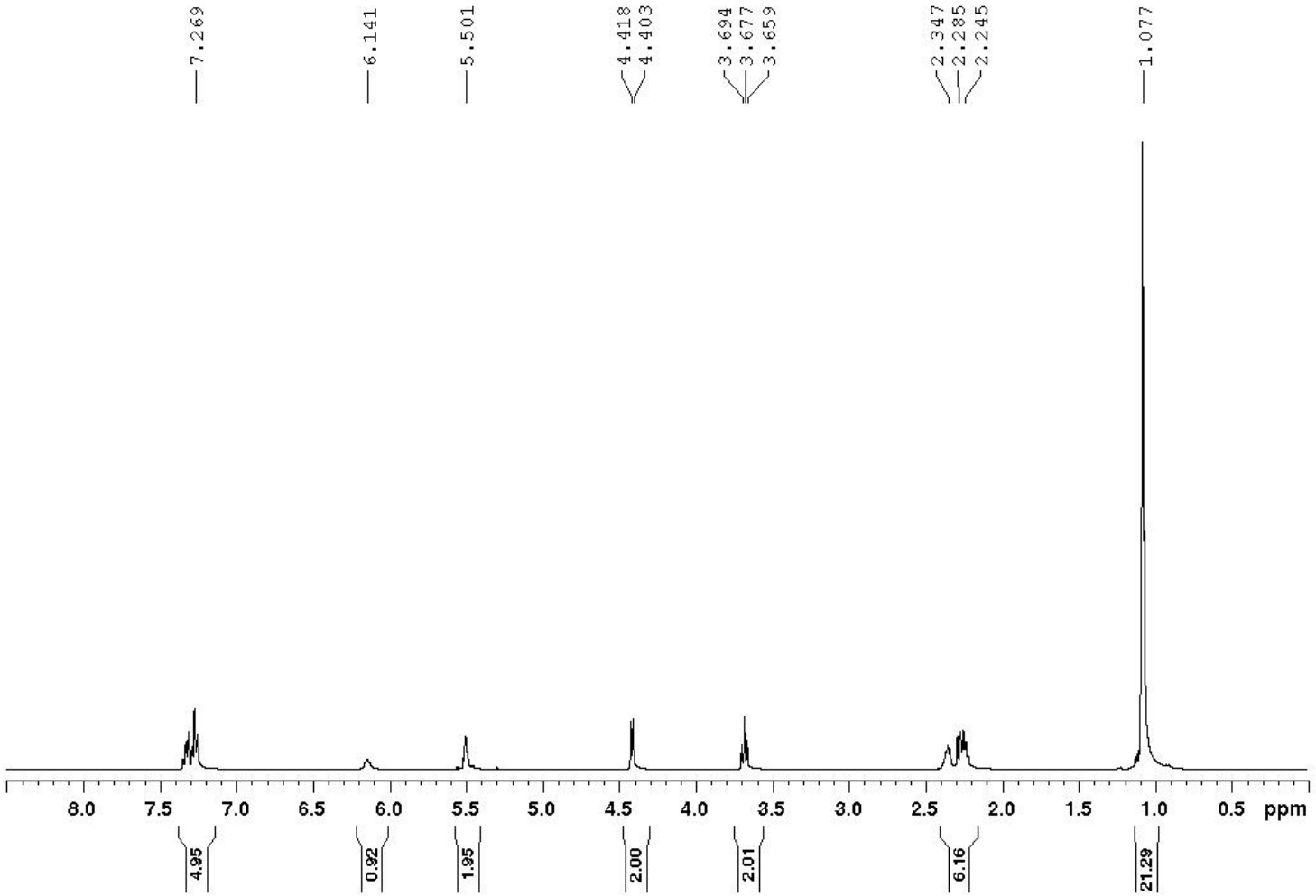


5k



TLC analysis	R_f 0.5 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.20–7.40 (5H, m, a,b,b',c,c'), 6.14 (1H, br s, NH), 5.40–5.55 (2H, m, i,j), 4.41 (2H, d, *J* = 5.7 Hz, e), 3.67 (2H, t, *J* = 6.8 Hz, l), 2.20–2.40 (6H, m, g,h,k), 1.00–1.15 (21H, m, m,m',m'',n,n',n'')
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.55 (f), 138.55 (d), 130.49 (i), 128.75 (b,b'), 128.29 (j), 127.84 (c,c'), 127.51 (a), 63.44 (l), 43.61 (e), 36.52 (k), 36.50 (g), 28.85 (h), 18.14 (n,n',n''), 12.11 (m,m',m'')
IR (neat)	3283 (N-H stretch), 2942, 2864, 1644 (C=O stretch), 1545 (N-H bend), 1455, 1100, 881, 679 cm^{-1}
HRMS (ESI)	$C_{23}H_{39}NNaO_2Si$ (M+Na): 412.2648, found 412.2652 *m/z*

^{1}H NMR of 5k


7.269
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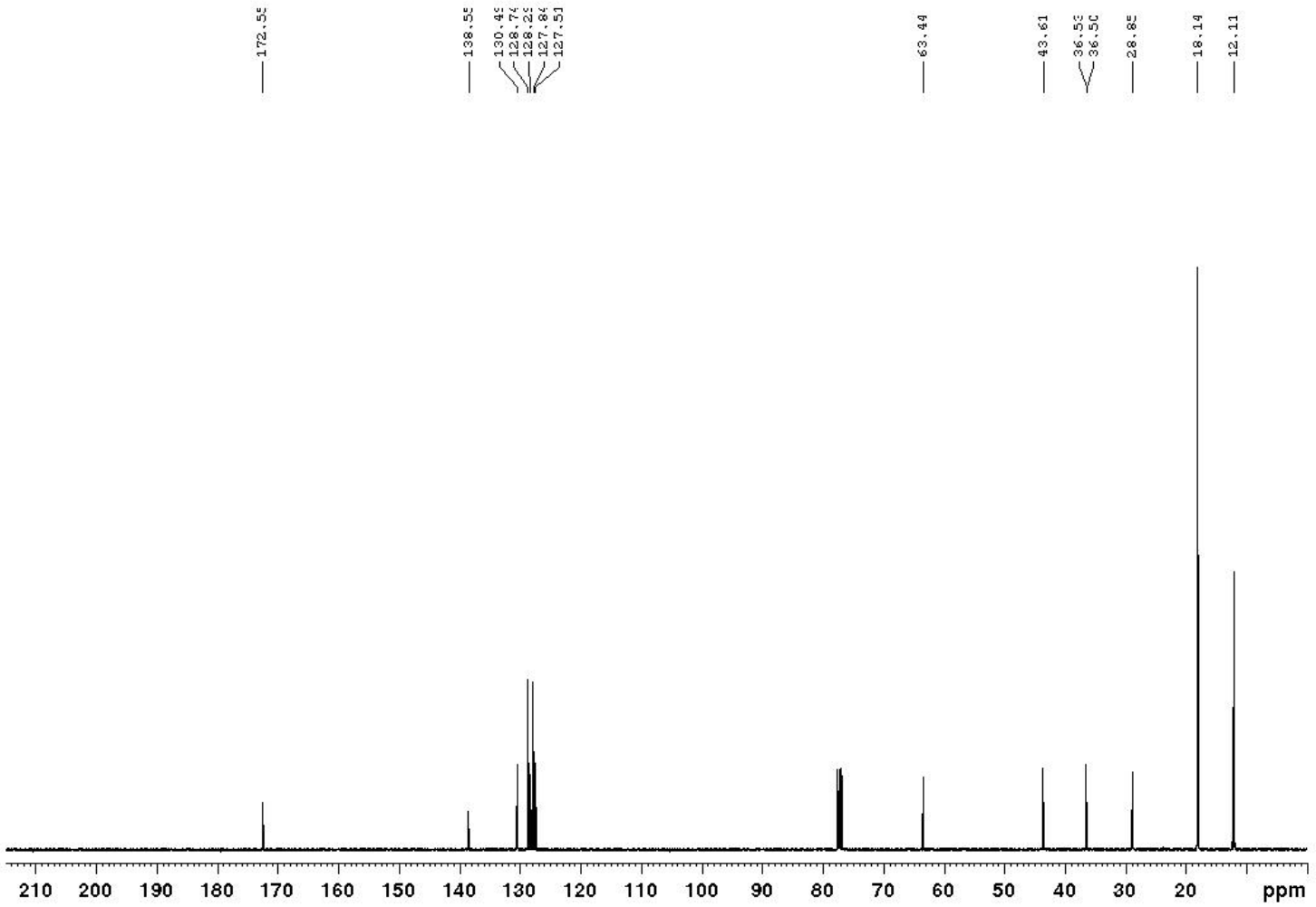
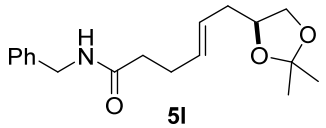
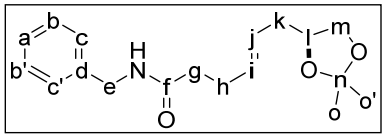
4.403
3.694
3.677
3.659
2.347
2.285
2.245
1.077
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.95
0.92
1.95
2.00
2.01
6.16
21.29

^{13}C NMR of 5k


172.55
138.55
130.49
128.74
128.25
127.84
127.51
63.49
43.61
36.53
36.50
28.85
18.14
12.11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

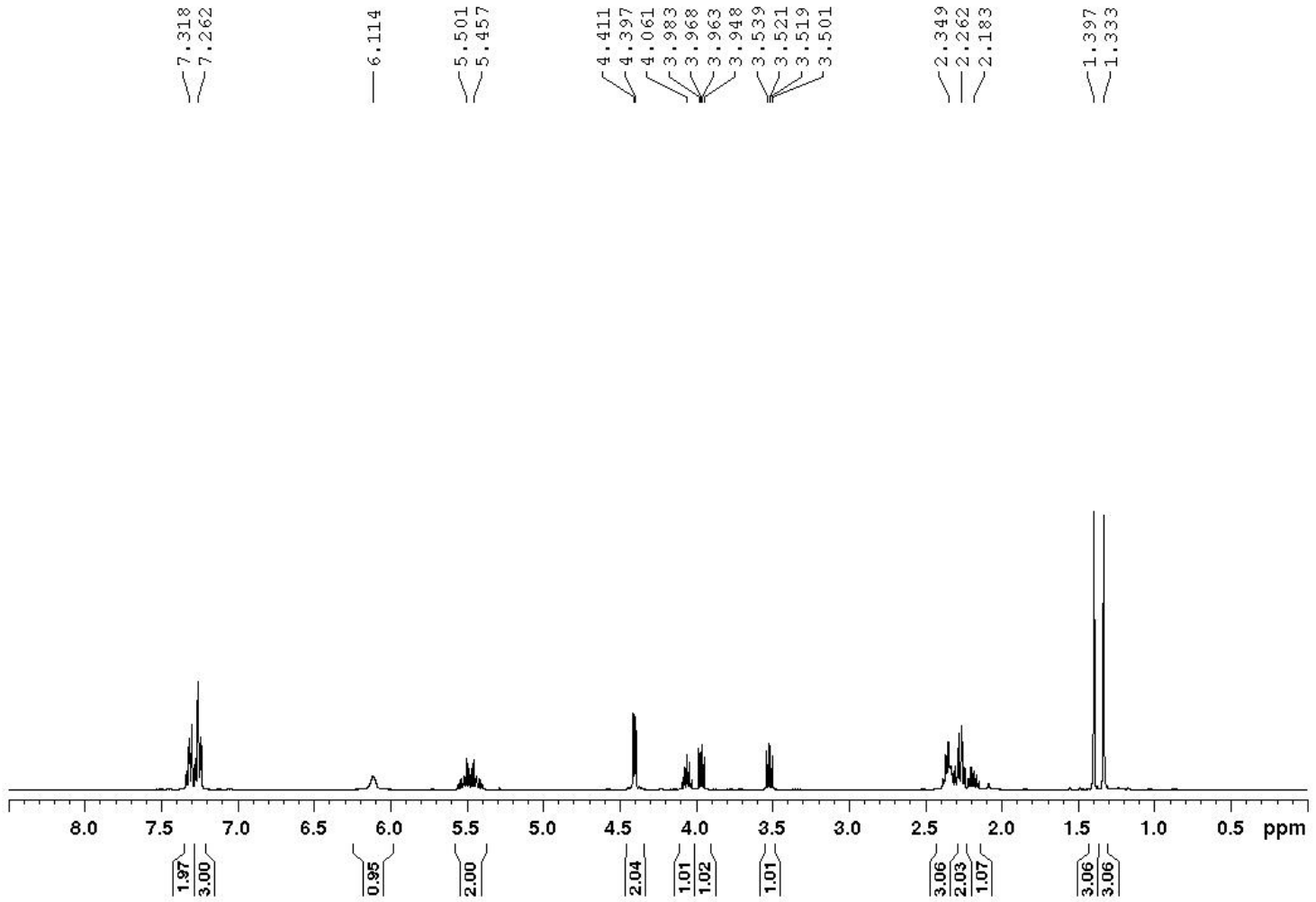


5l



$[\alpha]_D^{20}$	+19.2° (*c* 2.0, $CHCl_3$)
TLC analysis	R_f 0.25 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.35 (2H, m, b,b'), 7.20–7.30 (3H, m, a,c,c'), 6.11 (1H, br s, NH), 5.40–5.60 (2H, m, i,j), 4.40 (2H, d, *J* = 5.7 Hz, e), 4.00–4.10 (1H, m, l), 3.97 (1H, dd, *J* = 8.0 Hz, 6.0 Hz, m), 3.52 (1H, dd, *J* = 7.9 Hz, 7.0 Hz, m), 2.30–2.40 (3H, m, h,k), 2.25–2.30 (2H, m, g), 2.15–2.25 (1H, m, k), 1.40 (3H, s, o), 1.33 (3H, s, o')
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.32 (f), 138.53 (d), 131.82 (i), 128.76 (b,b'), 127.86 (c,c'), 127.54 (a), 126.52 (j), 109.00 (n), 75.53 (l), 68.92 (m), 43.60 (e), 36.92 (k), 36.37 (g), 28.70 (h), 27.01 and 25.74 (o,o')
IR (neat)	3291 (N-H stretch), 2984, 2933, 1643 (C=O stretch), 1541 (N-H bend), 1454, 1369, 1213, 1154, 1058, 969, 697 cm^{-1}
HRMS (ESI)	$C_{18}H_{25}NNaO_3$ (M+Na): 236.1732, found 326.1739 *m/z*

^{1}H NMR of 5l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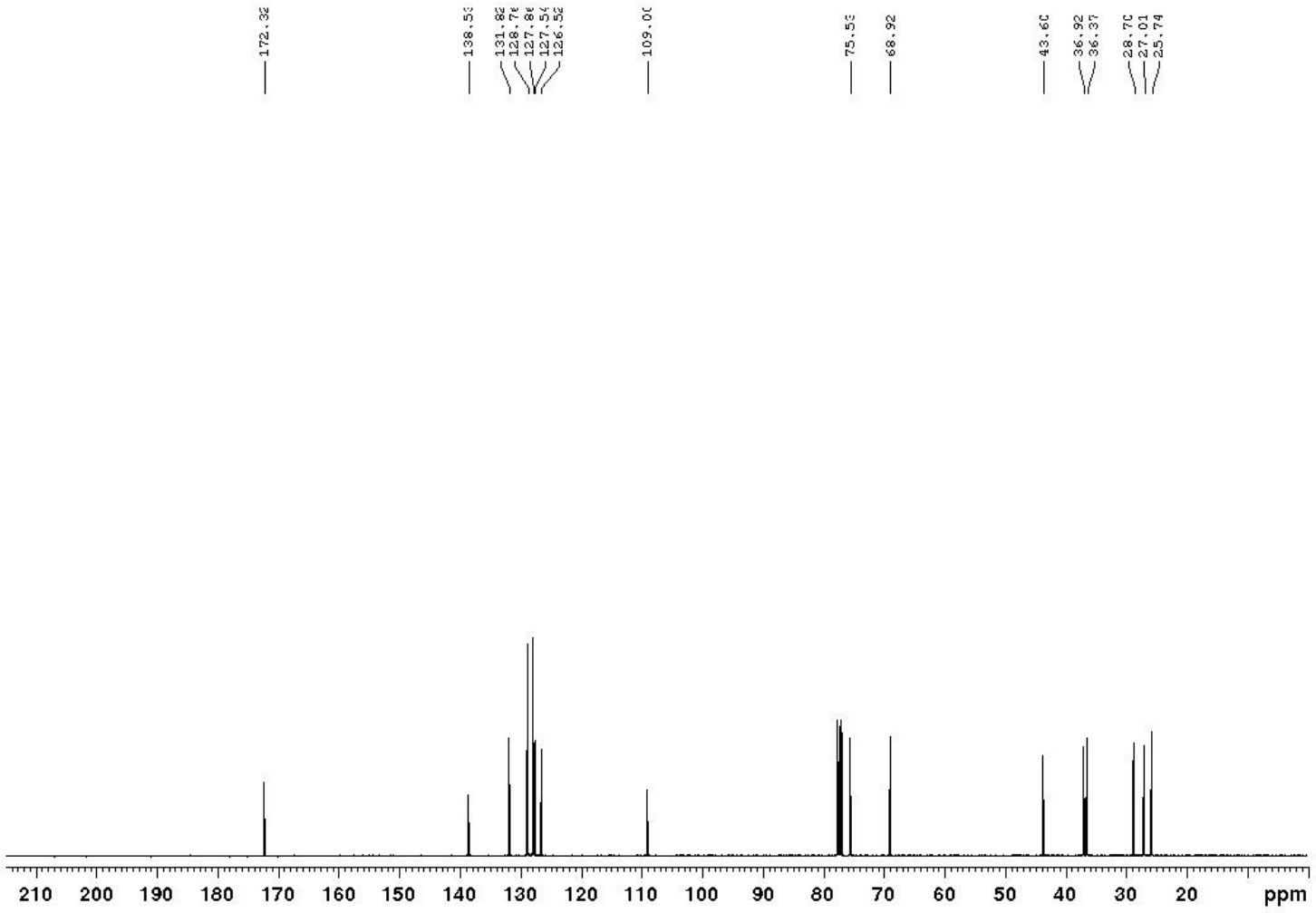
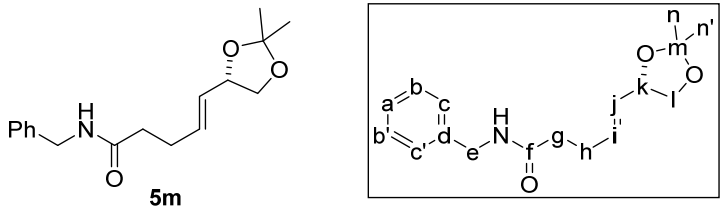
6.114
5.501
5.457
4.411
4.397
4.061
3.983
3.968
3.963
3.948
3.539
3.521
3.519
3.501
2.349
2.262
2.183
1.397
1.333
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.97
3.00
0.95
2.00
2.04
1.01
1.02
1.01
3.06
2.03
1.07
3.06
3.06

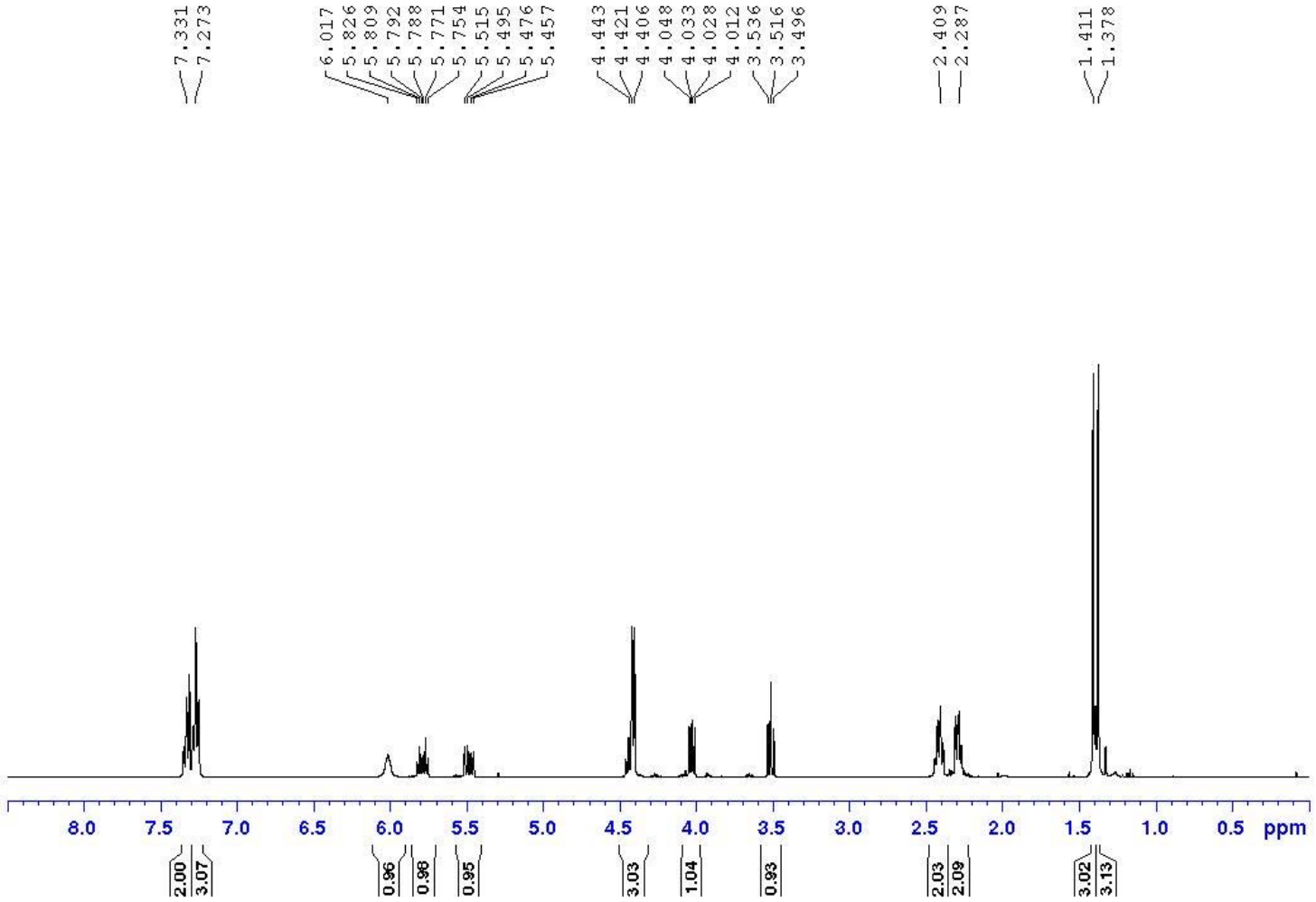
^{13}C NMR of 5l


172.32
138.53
131.82
128.78
127.84
127.54
126.52
109.00
75.53
68.92
43.60
36.92
36.37
28.70
27.01
25.74
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



$[\alpha]_D^{20}$	+25.1° (*c* 2.0, $CHCl_3$)
TLC analysis	R_f 0.25 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.35 (2H, m, b,b'), 7.25–7.30 (3H, m, a,c,c'), 6.02 (1H, br s, NH), 5.79 (1H, td, *J* = 15.3 Hz, 6.5 Hz, i), 5.49 (1H, dd, *J* = 15.4 Hz, 7.7 Hz, j), 4.35–4.50 (1H, m, k), 4.41 (2H, d, *J* = 5.7 Hz, e), 4.03 (1H, dd, *J* = 8.1 Hz, 6.1 Hz, l), 3.52 (1H, dd, *J* = 8.0 Hz, 8.0 Hz, l), 2.35–2.45 (2H, m, h), 2.25–2.35 (2H, m, g), 1.41 (3H, s, n), 1.38 (3H, s, n')
^{13}C NMR (100 MHz, $CDCl_3$)	δ 171.96 (f), 138.41 (d), 133.72 (i), 128.80 (b,b'), 128.77 (j), 127.91 (c,c'), 127.62 (a), 109.25 (m), 69.48 (k), 43.68 (e), 35.84 (g), 28.23 (h), 26.83 and 26.01 (n,n')
IR (neat)	3294 (N-H stretch), 2985, 2933, 2872, 1644 (C=O stretch), 1541 (N-H bend), 1454, 1369, 1244, 1213, 1155, 1057, 1028, 967, 859, 732, 697 cm^{-1}
HRMS (ESI)	$C_{17}H_{23}NNaO_3$ (M+Na): 312.1576, found 312.1581 *m/z*.

^{1}H NMR of 5m


7.331
7.273
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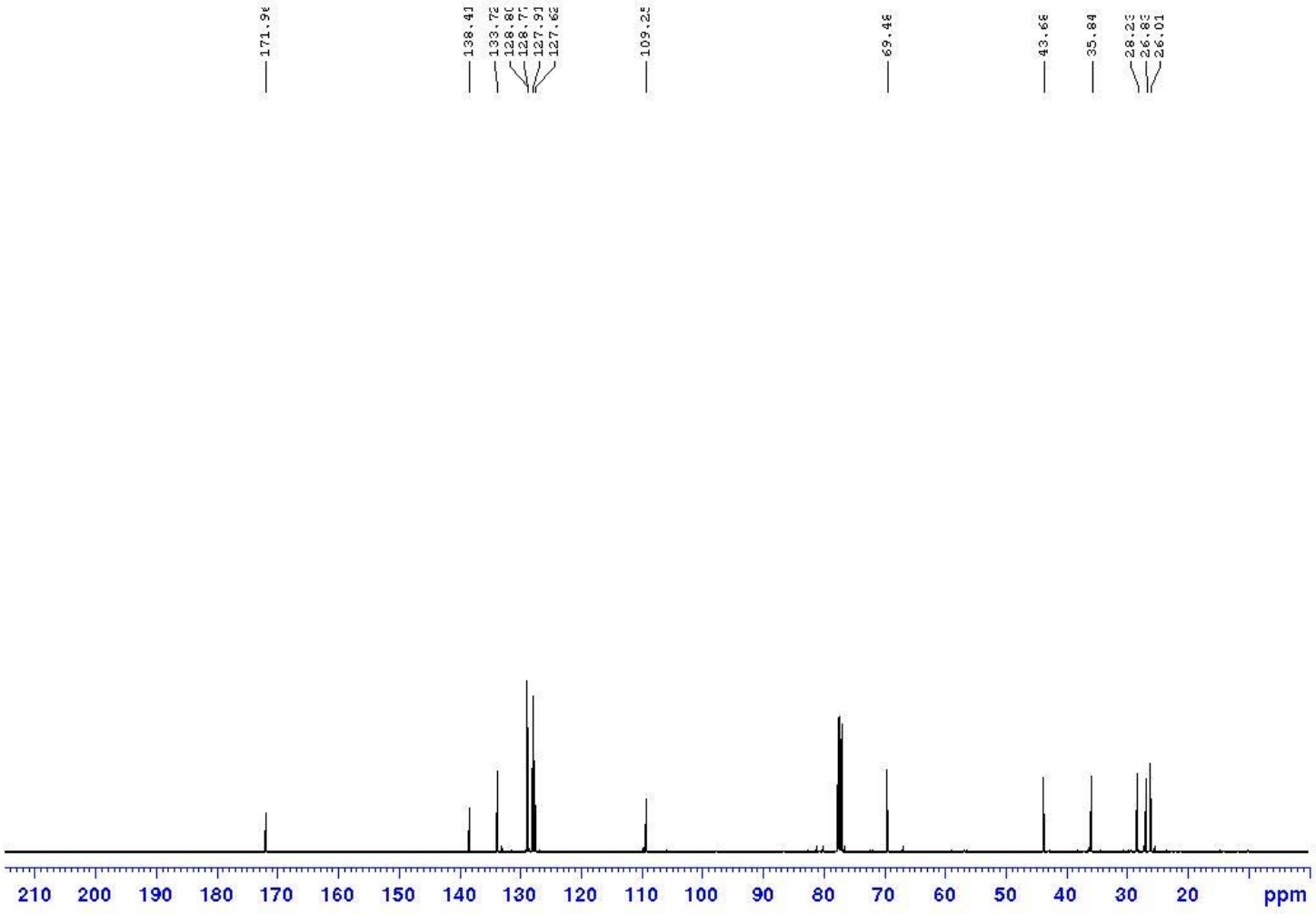
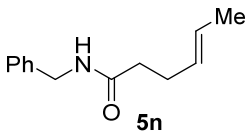
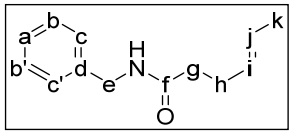
5.826
5.809
5.792
5.788
5.771
5.754
5.515
5.495
5.476
5.457
4.443
4.421
4.406
4.048
4.033
4.028
4.012
3.536
3.516
3.496
2.409
2.287
1.411
1.378
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
3.07
0.96
0.98
0.95
3.03
1.04
0.93
2.03
2.09
3.02
3.13

^{13}C NMR of 5m


171.9
138.41
133.72
128.80
128.71
127.91
127.62
109.25
69.48
43.66
35.84
28.23
26.83
26.01
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

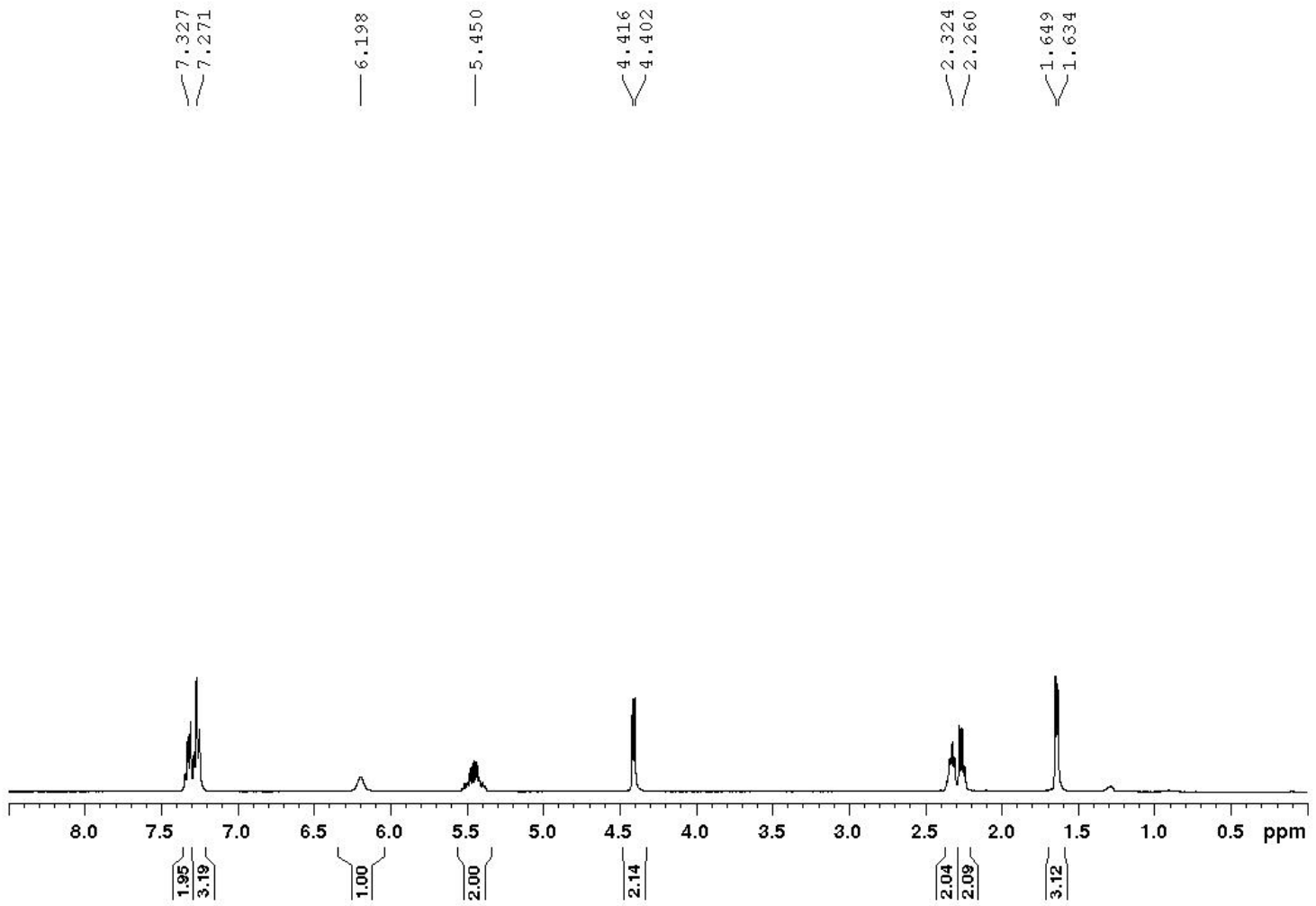


5n



m.p.	58.5–59.5 ºC
TLC analysis	R_f 0.40 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.35 (2H, m, b,b'), 7.20–7.30 (3H, m, a,c,c'), 6.20 (1H, br s, NH), 5.25–5.55 (2H, m, i,j), 2.30–2.35 (2H, m, h), 2.20–2.30 (2H, m, g), 1.64 (3H, d, *J* = 5.8 Hz, k)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.64 (f), 138.59 (d), 129.64 (i), 128.74 (b,b'), 127.85 (c,c'), 127.49 (a), 126.43 (j), 43.58 (e), 36.60 (g), 28.75 (h), 18.00 (k)
IR (neat)	3289 (N-H stretch), 2918, 1633 (C=O stretch), 1548 (N-H bend), 1493, 1452, 1234, 964, 747, 697 cm^{-1}
HRMS (ESI)	$C_{13}H_{17}NNaO$ (M+Na): 226.1208, found 226.1208 *m/z*

^{1}H NMR of 5n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4.402
2.324
2.260
1.649
1.634
8.0
7.5
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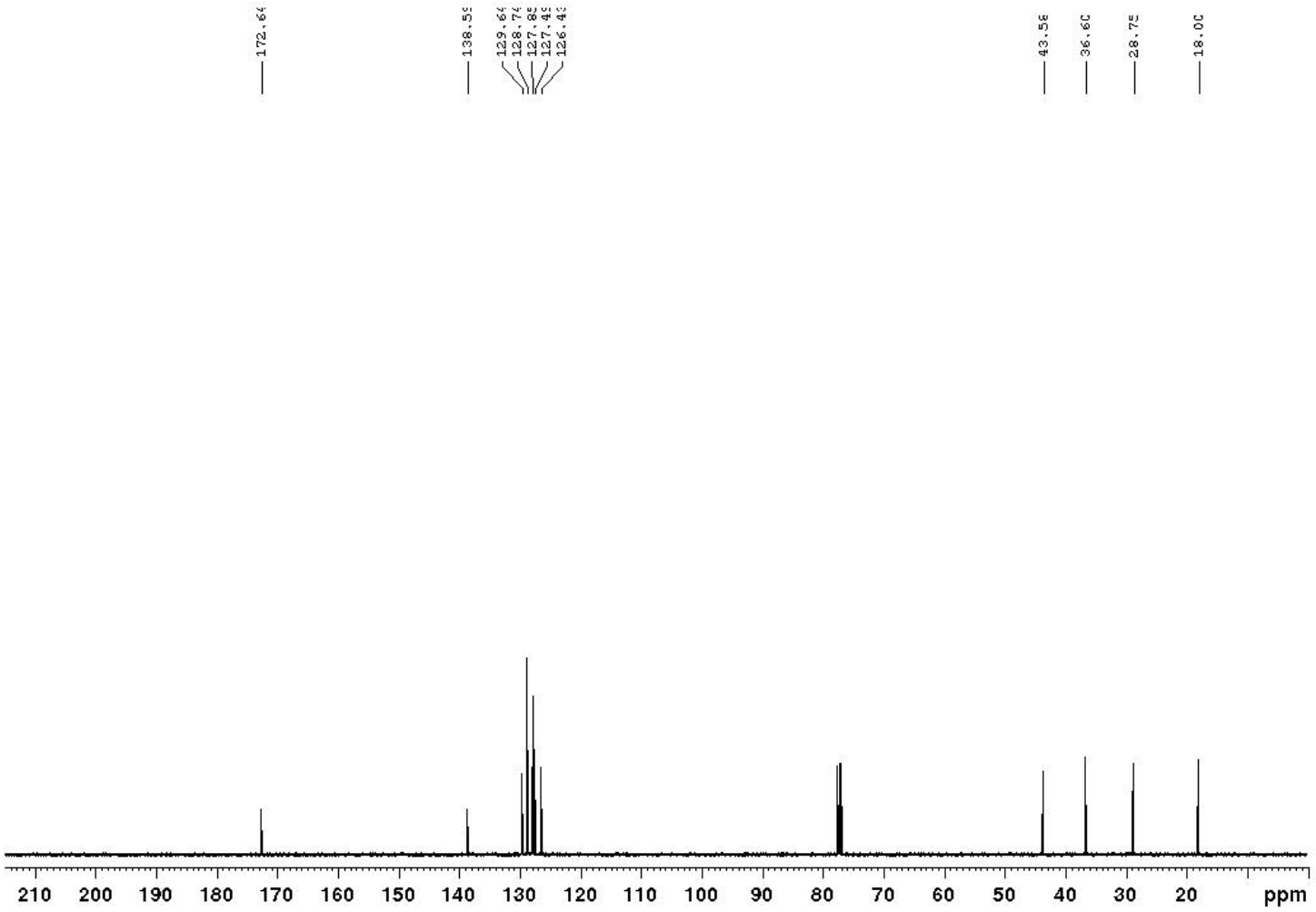
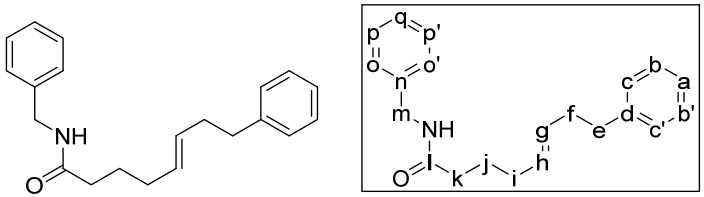
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.95
3.19
1.00
2.00
2.14
2.04
2.09
3.12

^{13}C NMR of 5n

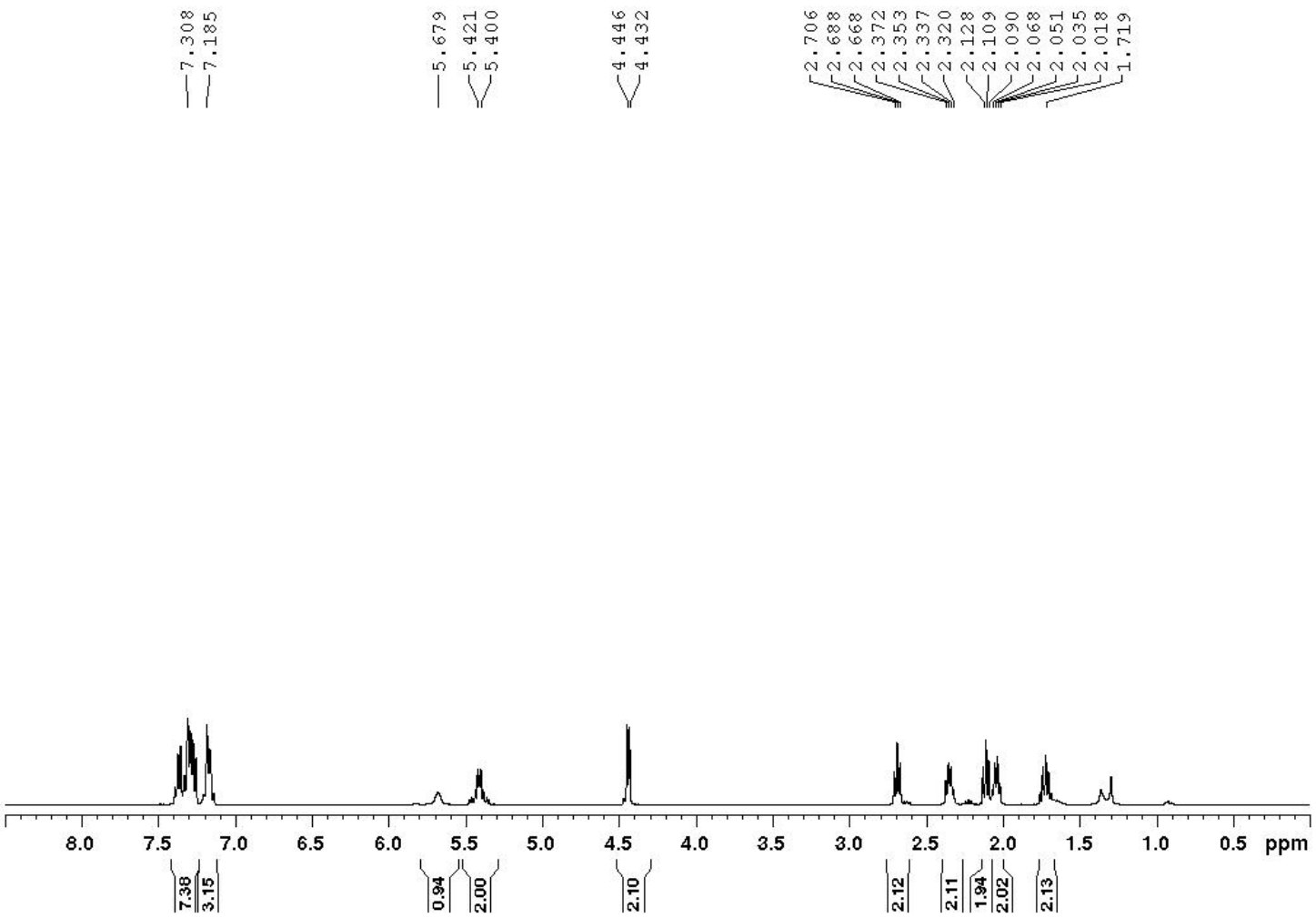

172.64
138.59
129.64
128.74
127.85
127.45
126.43
43.56
36.60
28.75
18.00
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



9

m.p.	67.0–68.0 ºC
TLC analysis	R_f 0.40 (60:40 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.40 (7H, m, b,b',o,o',p,p',q), 7.15–7.25 (3H, m, a,c,c'), 5.68 (1H, br s, NH), 5.30–5.50 (2H, m, g,h), 4.44 (2H, d, *J* = 5.7 Hz, m), 2.69 (2H, t, *J* = 7.4 Hz, e), 2.34 (2H, q, *J* = 6.6 Hz, f), 2.11 (2H, t, *J* = 7.4 Hz, k), 2.04 (2H, q, *J* = 6.6 Hz, i), 1.65–1.80 (2H, m, j)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.92 (l), 142.08 (d), 138.54 (n), 130.66 (g), 130.17 (h), 128.83 (b,b'), 128.64 (p,p'), 128.37 (c,c'), 128.00 (o,o'), 127.64 (q), 125.84 (a), 43.70 (m), 36.95 (e), 35.80 (k), 34.19 (f), 31.95 (i), 25.37 (j)
IR (neat)	3290 (N-H stretch), 2924, 2848, 1629 (C=O stretch), 1550 (N-H bend), 1494, 1452, 726, 693 cm^{-1}
HRMS (ESI)	$C_{21}H_{25}NNaO$ (M+Na): 330.1834, found 330.1833 *m/z*

^{1}H NMR of 9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2.706
2.688
2.668
2.372
2.353
2.337
2.320
2.128
2.109
2.090
2.068
2.051
2.035
2.018
1.719
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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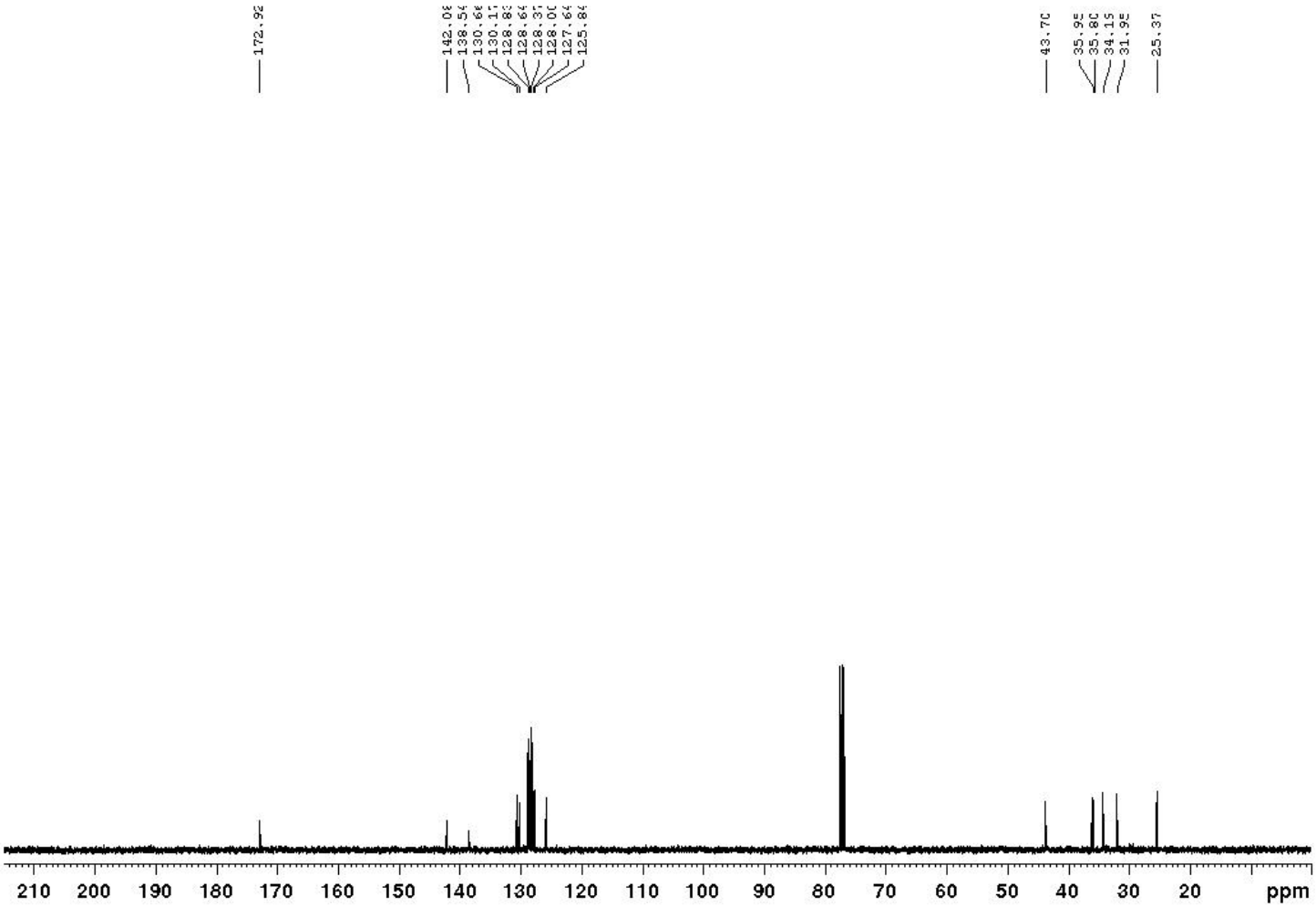
2.00
2.10
2.12
2.11
1.94
2.02
2.13

^{13}C NMR of 9


172.92
142.08
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130.66
130.11
128.85
128.64
128.37
128.00
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125.84
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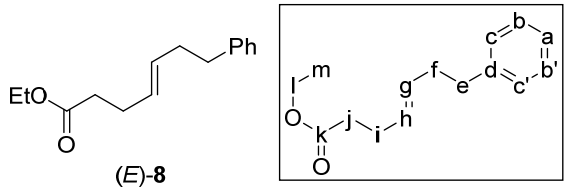
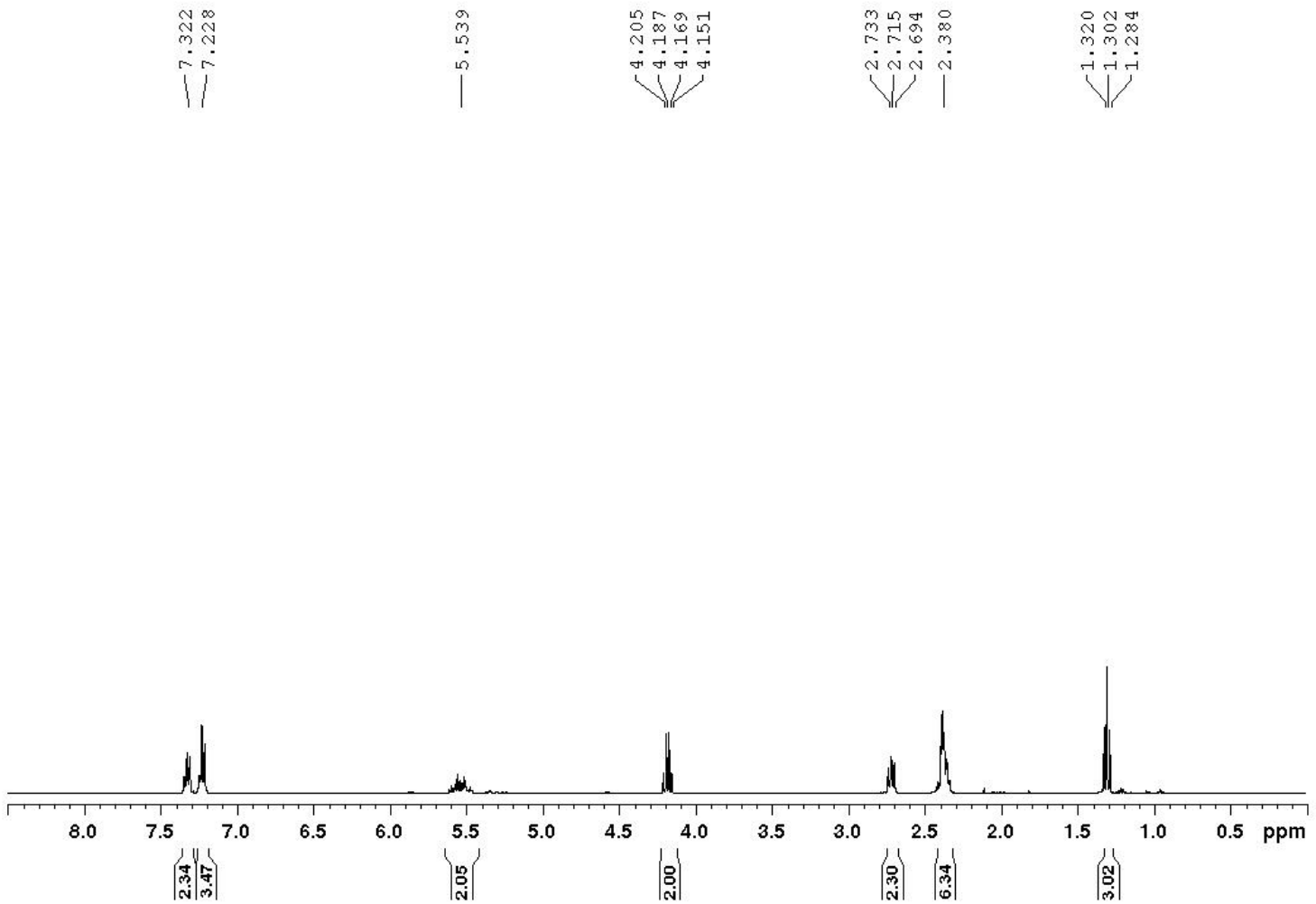
35.95
35.80
34.15
31.95
25.37
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



TLC analysis	R_f 0.4 (90:10 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.35 (2H, m, b,b'), 7.30–7.35 (3H, m, a,c,c'), 5.45–5.60 (2H, m, g,h), 4.18 (2H, q, *J* = 7.1 Hz,, l), 2.72 (2H, t, *J* = 7.3 Hz, e), 2.30–2.40 (6H, m, f,i,j), 1.30 (3H, t, *J* = 7.1 Hz, m)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.27 (k), 142.07 (d), 130.85 (h), 128.96 (g), 128.59 (b,b'), 128.39 (c,c'), 125.90 (a), 60.35 (l), 36.09 (e), 34.49 (j), 34.44 (f), 28.04 (i), 14.42 (m)
IR (neat)	2980, 2925, 1732 (C=O stretch), 1453, 1371, 1247, 1175, 1032, 968, 745, 698 cm^{-1}
HRMS (ESI)	$C_{15}H_{20}NaO_2$ (M+Na): 255.1361, found 255.1364 *m/z*

^{1}H NMR of (*E*)-8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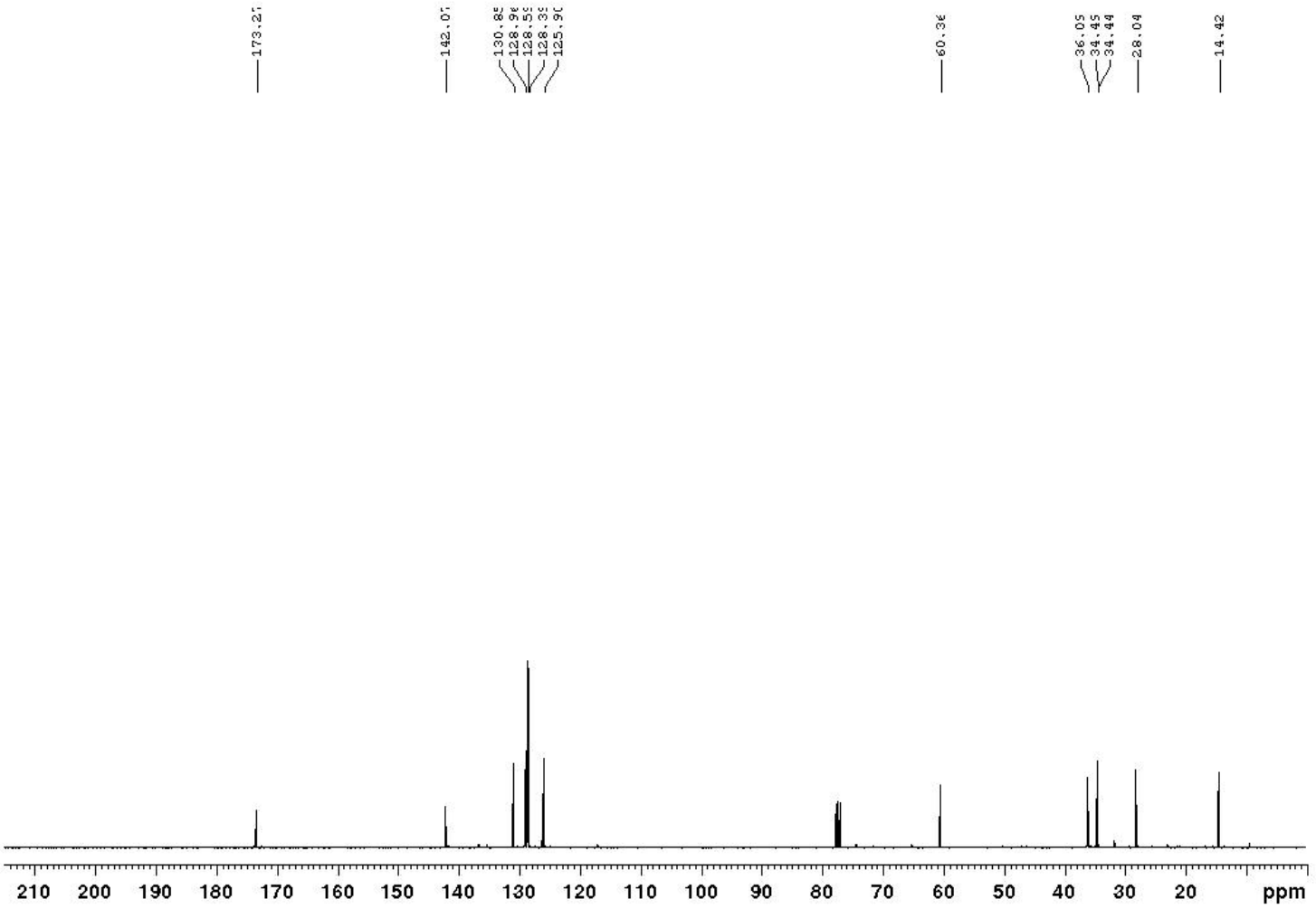
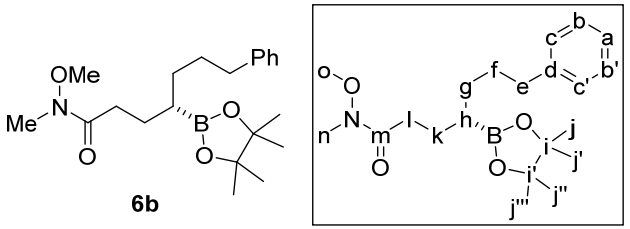
7.228
5.539
4.205
4.187
4.169
4.151
2.733
2.715
2.694
2.380
1.320
1.302
1.284
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.34
3.47
2.05
2.00
2.30
6.34
3.02

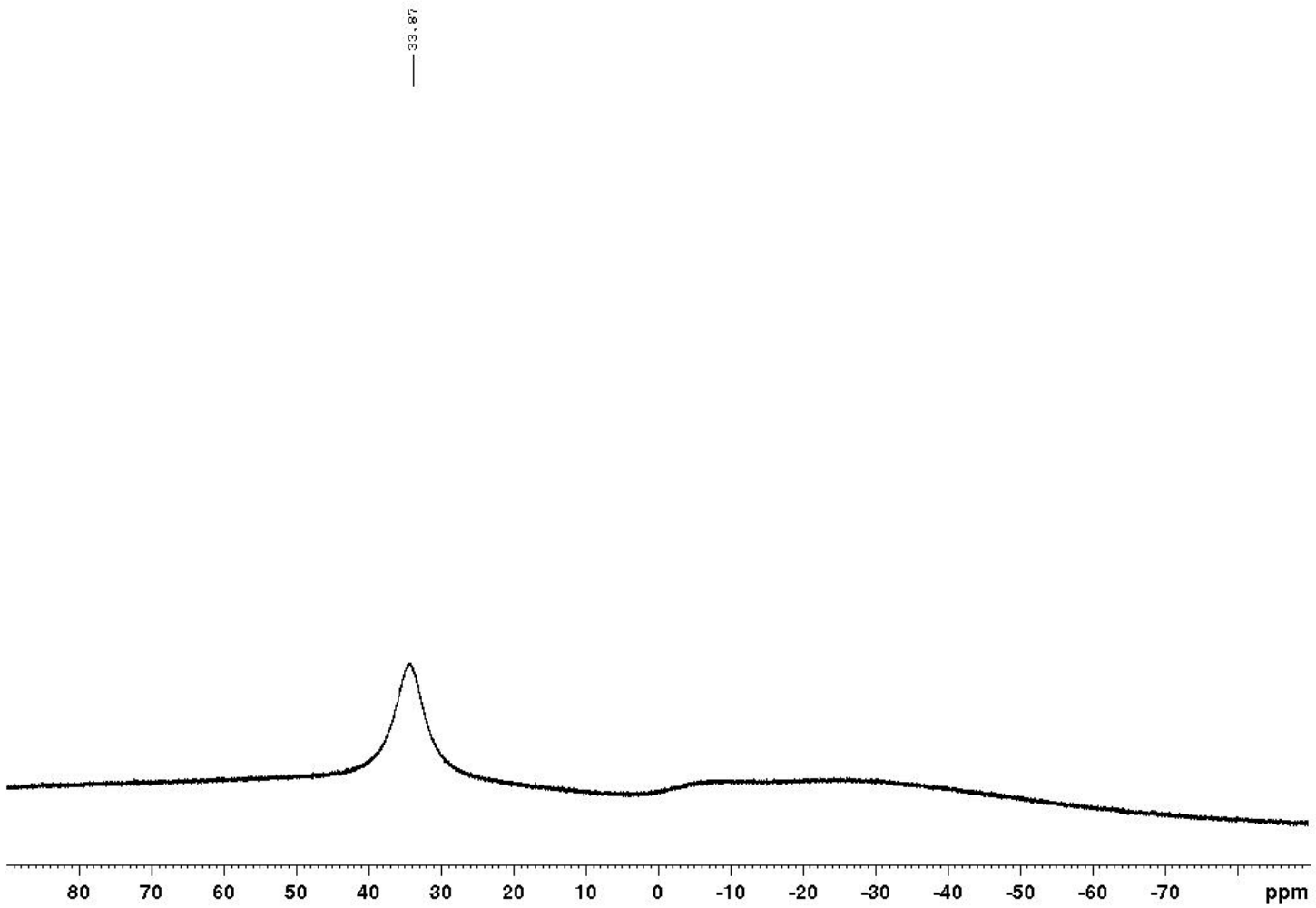
^{13}C NMR of (*E*)-8


173.27
142.07
130.85
128.98
128.58
128.38
125.90
60.36
36.05
34.45
34.44
28.04
14.42
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

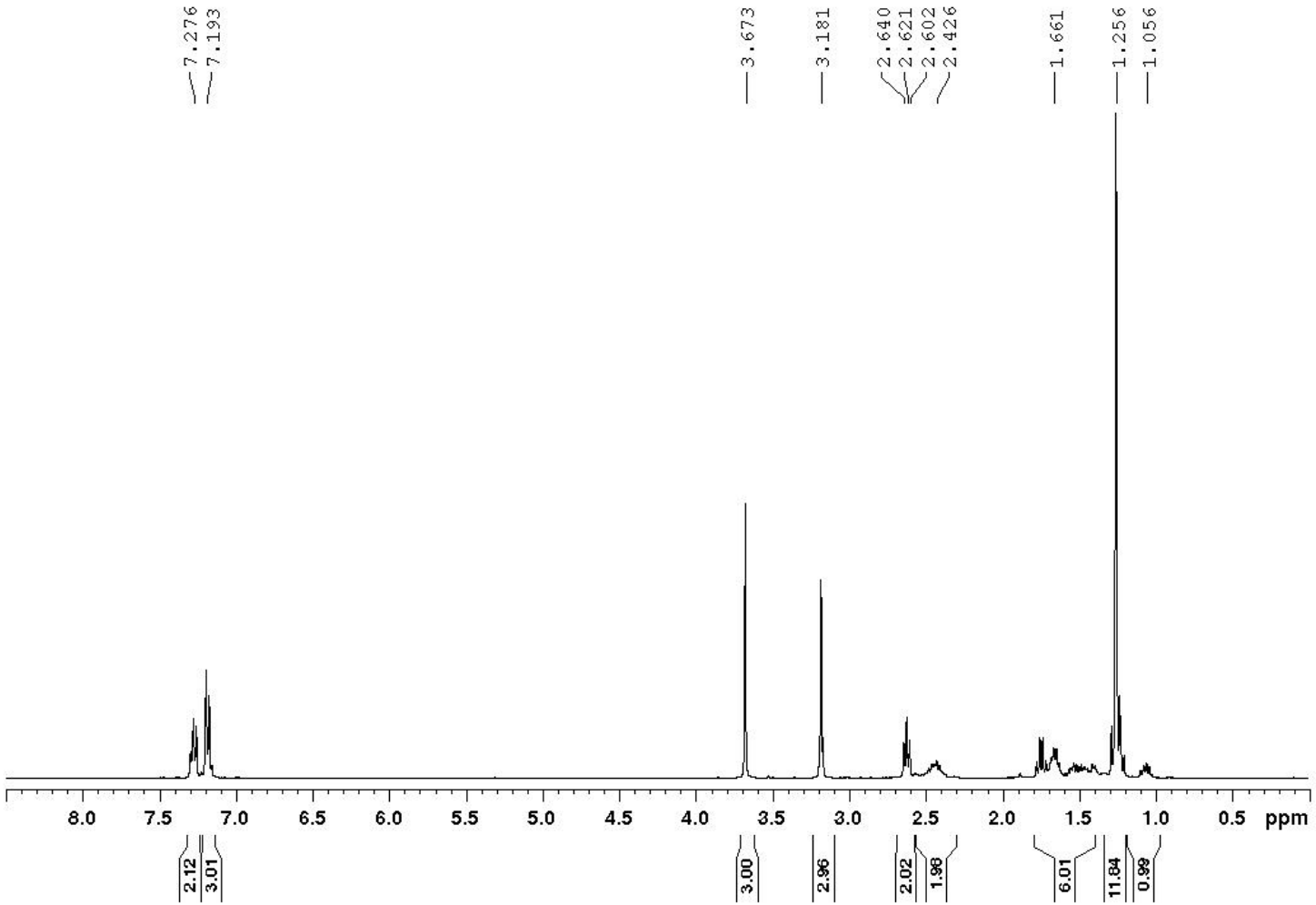


$[\alpha]_D^{20}$	+5.1° (*c* 2.0, $CHCl_3$)
TLC analysis	R_f 0.4 (60:40 hexanes:ethyl acetate)
^{11}B NMR (128 MHz, $CDCl_3$)	δ 33.87
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.30 (2H, m, b,b'), 7.15–7.25 (3H, m, a,c,c'), 3.67 (3H, s, o), 3.18 (3H, s, n), 2.62 (2H, d, *J* = 7.6 Hz, e), 2.30–2.60 (2H, m, l), 1.40–1.80 (6H, m, f,g,k), 1.26 (12H, s, j,j',j'',j'''), 1.00–1.15 (1H, m, h)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 174.93 (m), 142.89 (d), 128.50 (b,b'), 128.31 (c,c'), 125.63 (a), 83.09 (i,i'), 61.29 (o), 36.30 (e), 32.28 (n), 31.71 (l), 31.01 (f), 31.00 (g), 26.30 (k), 24.97 and 24.93 (j,j',j'',j''')
IR (neat)	2976, 2930, 2857, 1663 (C=O stretch), 1380 (C-N stretch), 1314, 1142 , 699 cm^{-1}
HRMS (ESI)	$C_{21}H_{34}BNNaO_4$ (M+Na): 398.2479, found 398.2496 *m/z*

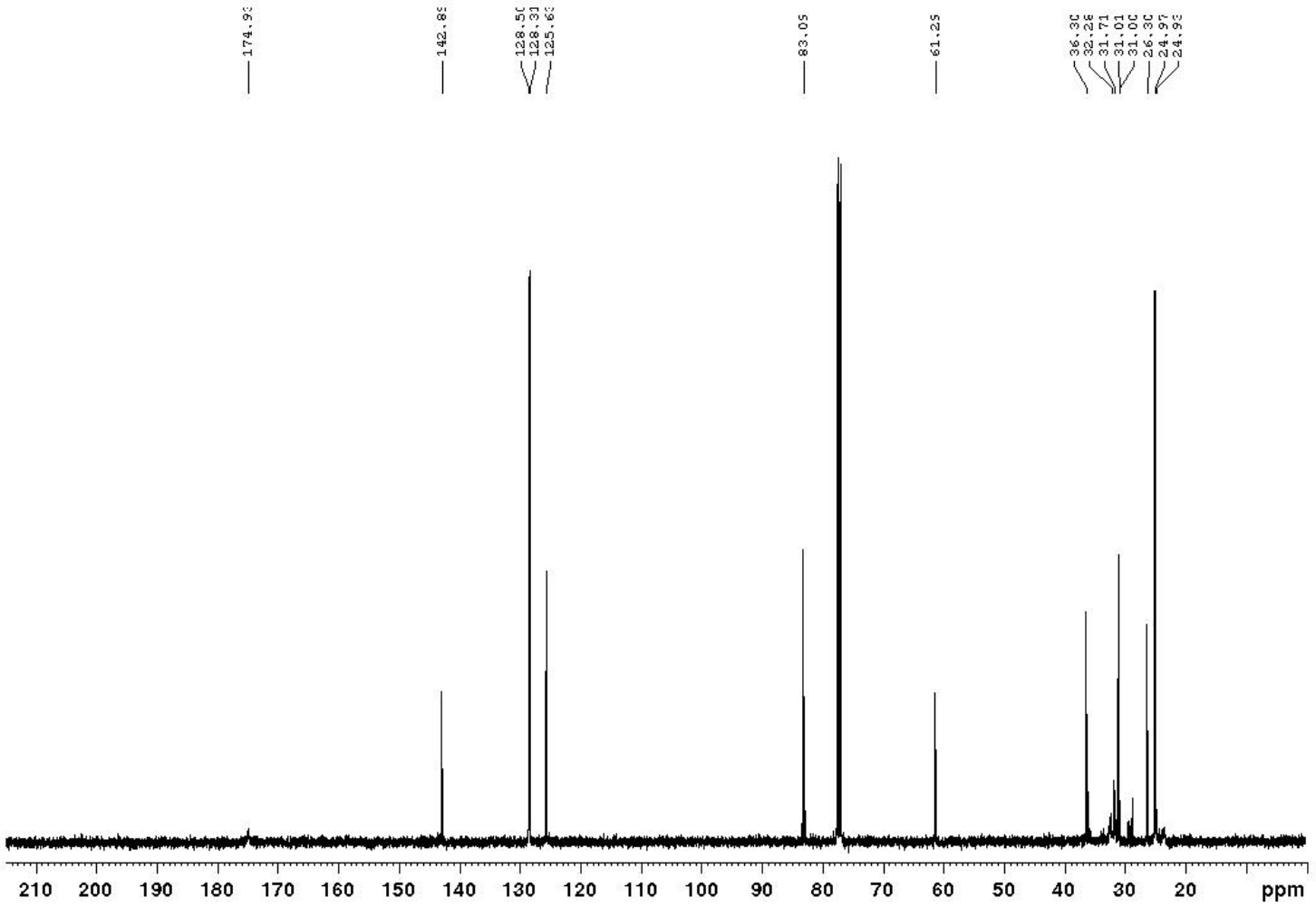
^{11}B NMR of 6b

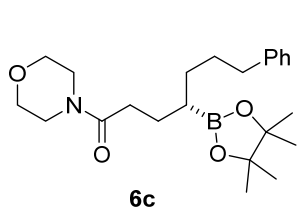


^{1}H NMR of 6b

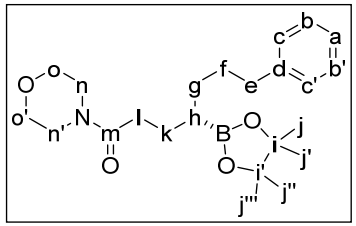

7.276
7.193
3.673
3.181
2.640
2.621
2.602
2.426
1.661
1.256
1.056
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.12
3.01
3.00
2.96
2.02
1.96
6.01
11.84
0.99

^{13}C NMR of 6b


174.9
142.8
128.5
128.3
125.6
83.05
61.25
36.3
32.2
31.7
31.0
31.0
26.3
24.9
24.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

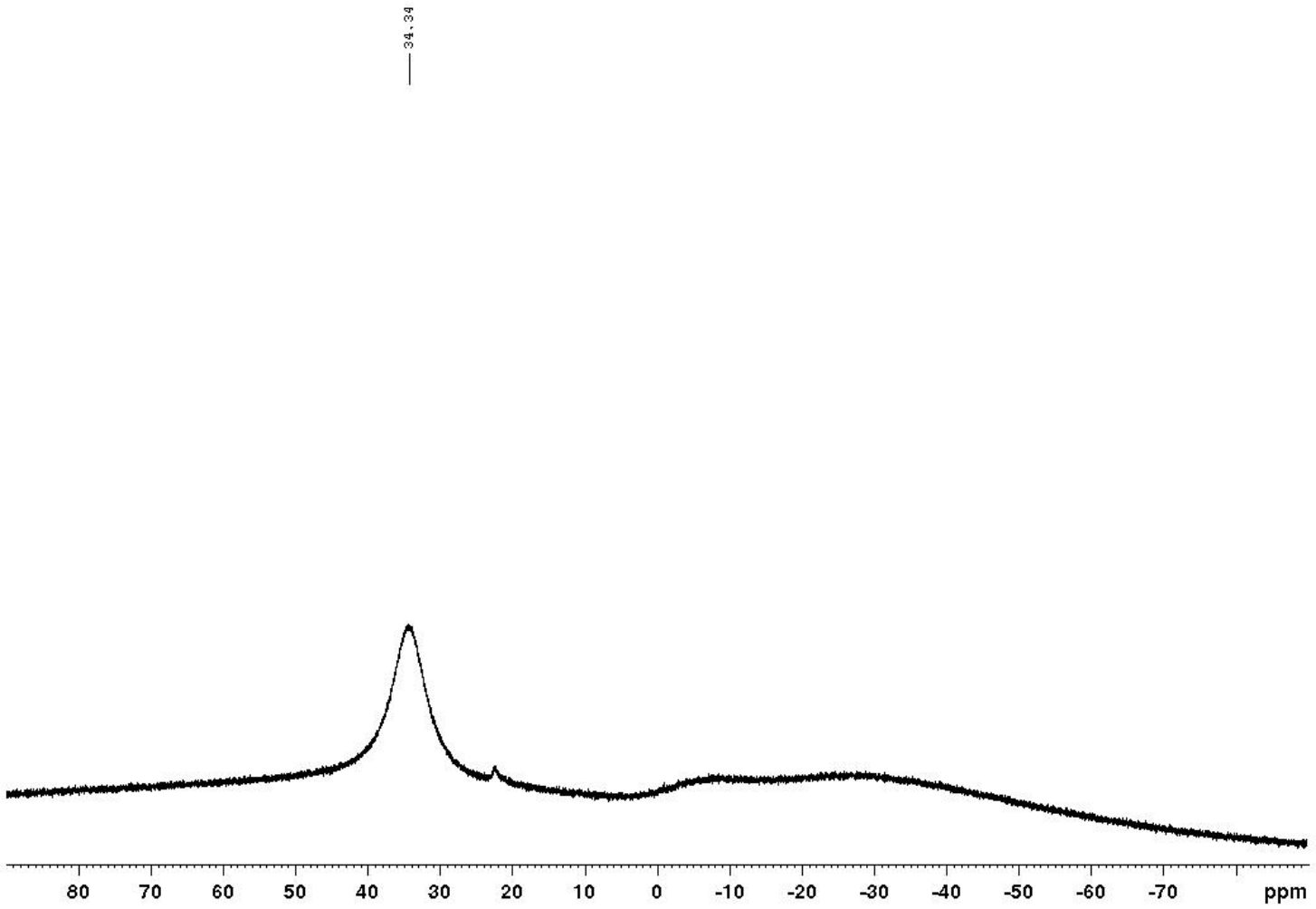


6c

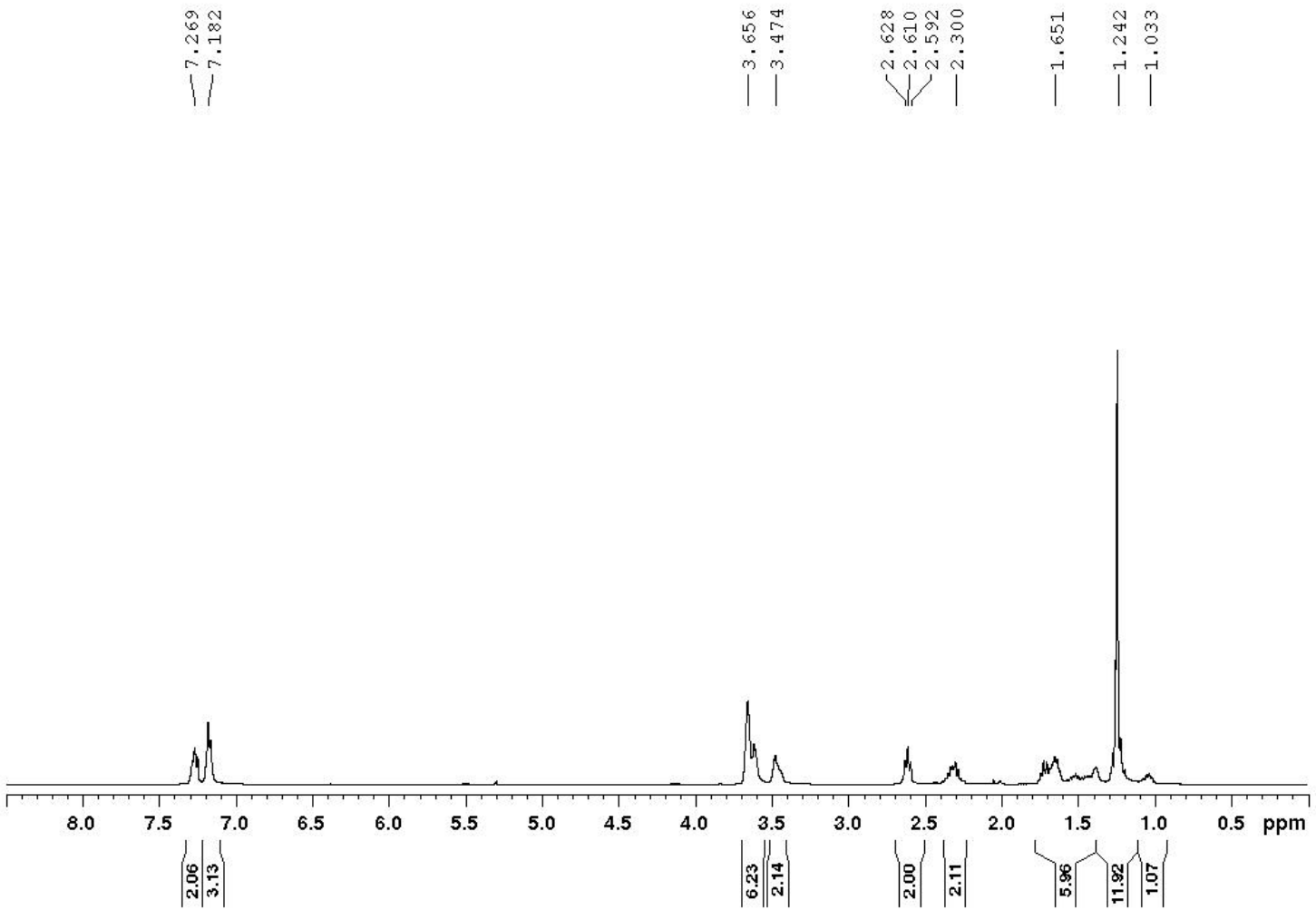


$[\alpha]_D^{20}$	+0.3° (*c* 2.0, $CHCl_3$)
TLC analysis	δ 34.34
^{11}B NMR (128 MHz, $CDCl_3$)	R_f 0.4 (40:60 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.35 (2H, m, b,b'), 7.10–7.25 (3H, m, a,c,c'), 3.55–3.70 (6H, m, n,n',o,o'), 3.40–3.50 (2H, m, n,n'), 2.61 (2H, d, *J* = 7.2 Hz, e), 2.25–2.40 (2H, m, l), 1.40–1.80 (6H, m, f,g,k), 1.24 (12H, s, j,j',j'',j'''), 1.00–1.10 (1H, m, h)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.11 (m), 144.78 (d), 128.49 (b,b'), 128.32 (c,c'), 125.67 (a), 83.17 (i,i'), 67.06 and 66.86 (o,o'), 46.19 and 41.95 (n.n'), 36.25 (e), 33.08 (l), 30.92 (f), 30.89 (g), 26.99 (k), 25.00 and 24.94 (j,j',j'',j''')
IR (neat)	2974, 2924, 2854, 1644 (C=O stretch), 1425 1380 (C-N stretch), 1142, 1114, 699 cm^{-1}
HRMS (ESI)	$C_{23}H_{36}BNNaO_4$ (M+Na): 424.2635, found 424.2648 *m/z*.

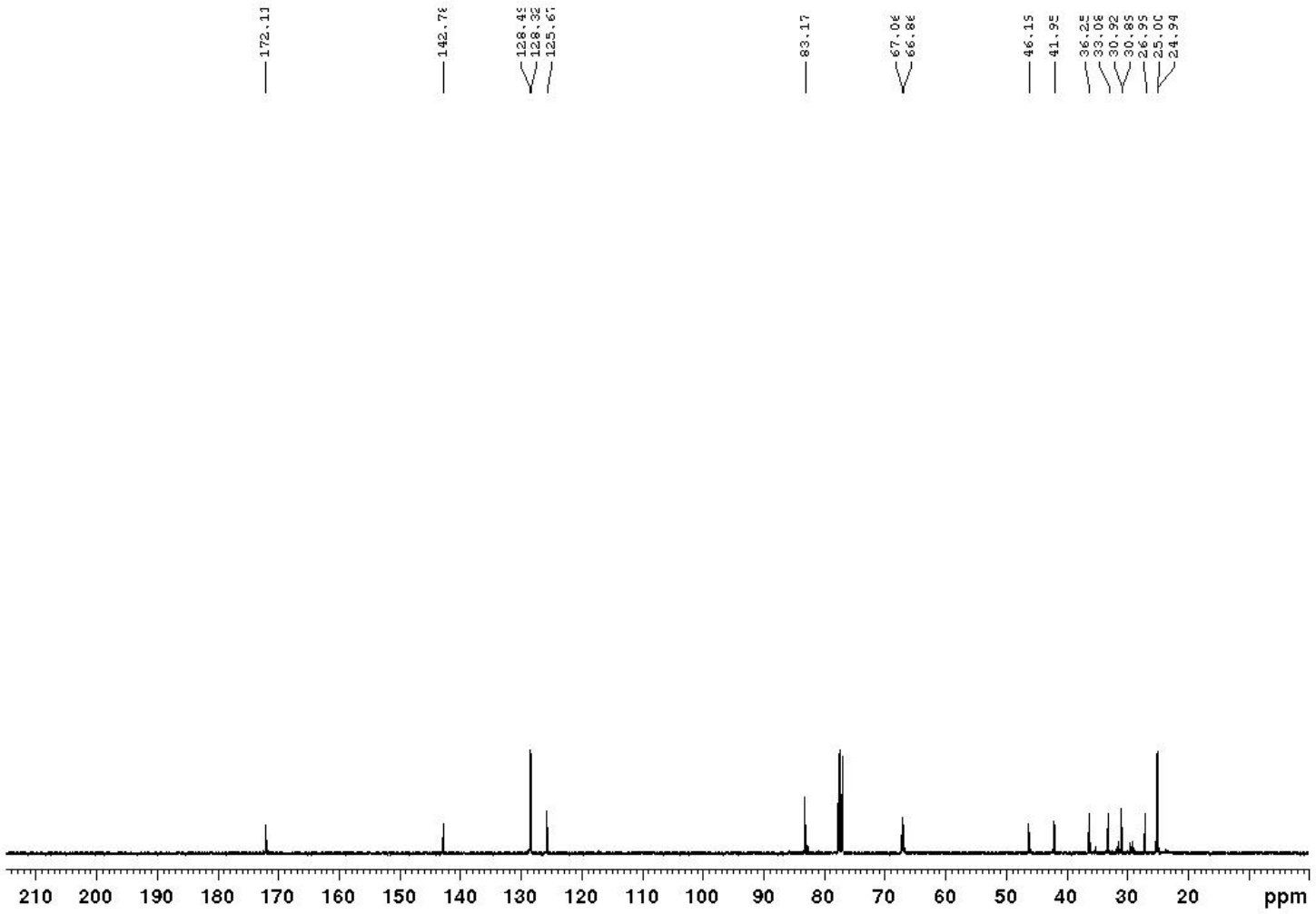
^{11}B NMR of 6c

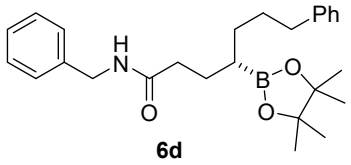


^{1}H NMR of 6c

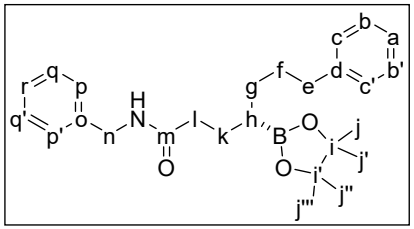

7.269
7.182
3.656
3.474
2.628
2.610
2.592
2.300
1.651
1.242
1.033
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.06
3.13
6.23
2.14
2.00
2.11
5.96
11.92
1.07

^{13}C NMR of 6c


172.11
142.78
128.45
128.38
125.67
83.17
67.06
66.84
46.15
41.95
36.25
33.06
30.92
30.85
26.95
25.00
24.94
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

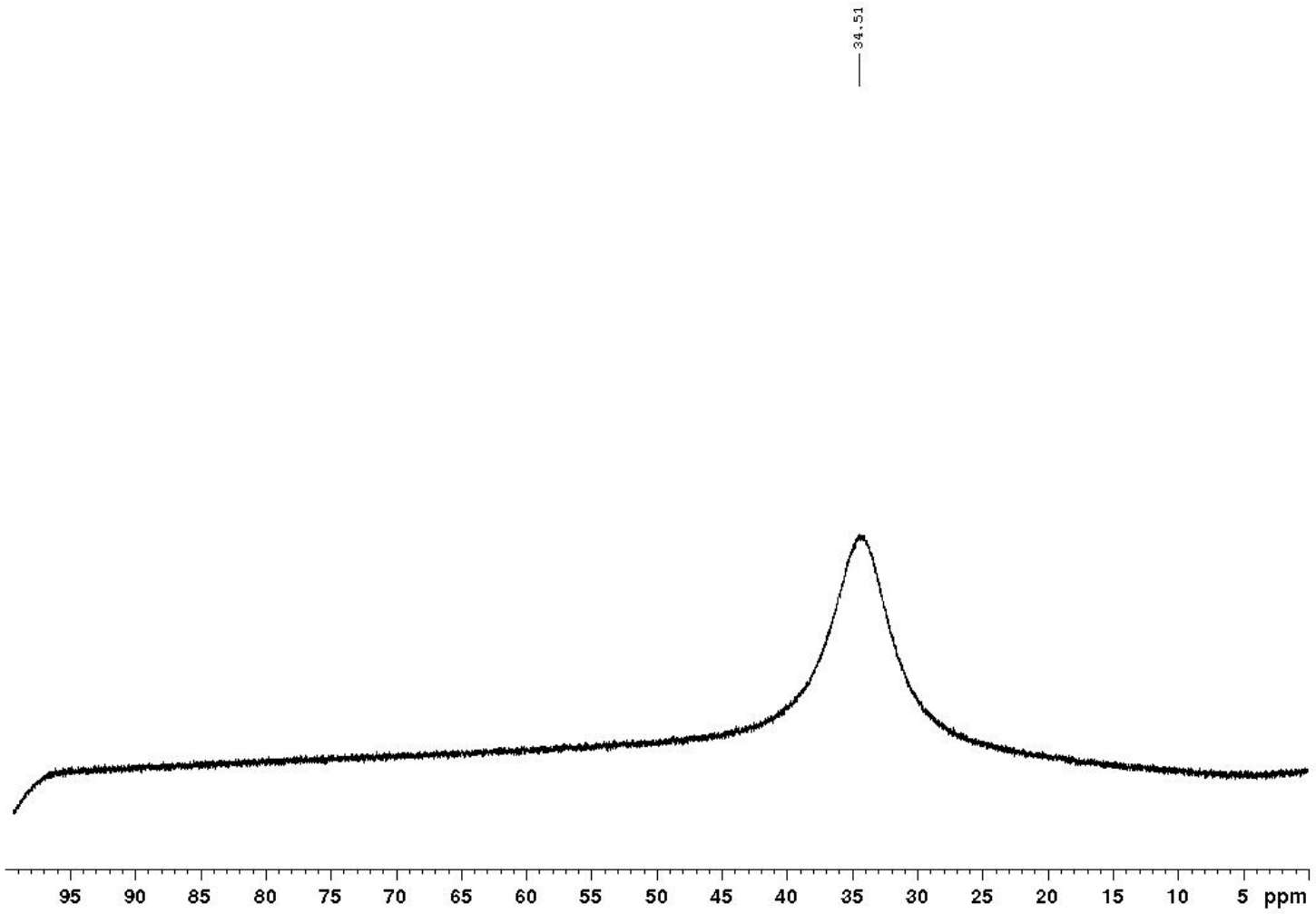


6d

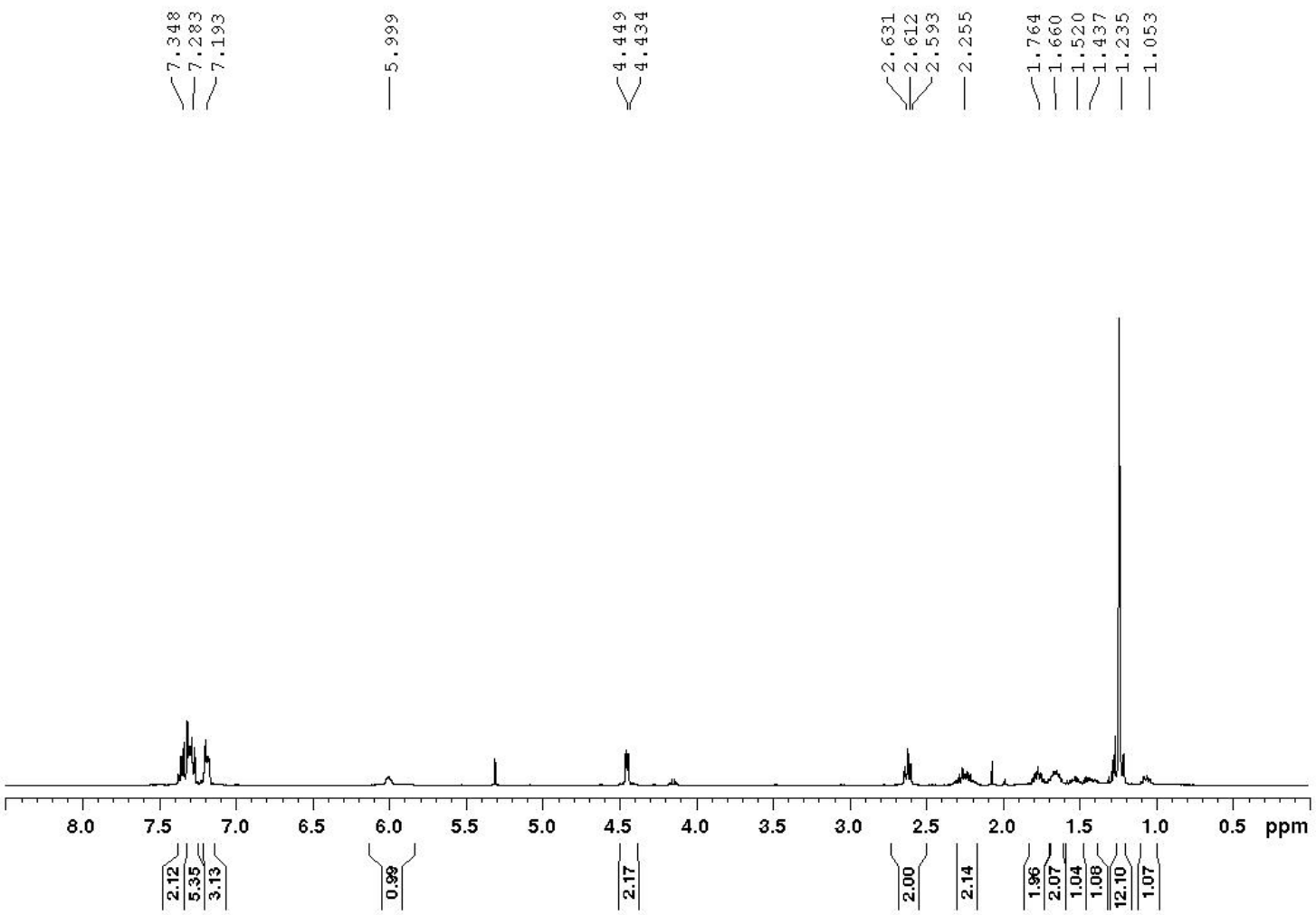


$[\alpha]_D^{20}$	+2.4° (*c* 2.0, $CHCl_3$)
TLC analysis	R_f 0.3 (60:40 hexanes:ethyl acetate)
^{11}B NMR (128 MHz, $CDCl_3$)	δ 34.51
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.40 (2H, m, q,q'), 7.25–7.30 (5H, m, b,b',c,c',r), 7.15–7.25 (3H, m, a,p,p'), 6.00 (1H, br s, NH), 4.44 (2H, d, *J* = 5.8 Hz, n), 2.61 (2H, t, *J* = 7.6 Hz, e), 2.15–2.30 (2H, m, l), 1.70–1.85 (2H, m, k), 1.60–1.70 (2H, m, f), 1.50–1.60 (1H, m, g), 1.40–1.50 (1H, m, g), 1.23 (12H, s, j,j',j'',j'''), 1.00–1.10 (1H, m, h)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.19 (m), 142.82 (d), 138.60 (o), 128.78 (q,q'), 128.51 (b,b'), 128.34 (c,c'), 128.00 (p,p'), 127.55 (r), 125.69 (a), 83.25 (i,i'), 43.72 (n), 36.50 (l), 36.26 (e), 30.98 (f), 30.94 (g), 27.49 (k), 24.95 (j,j',j'',j''')
IR (neat)	3285 (N-H stretch), 2976, 2926, 2856, 1644 (C=O stretch), 1541 (N-H bend), 1454, 1379 (C-N stretch), 1315, 1141, 747, 697 cm^{-1}
HRMS (ESI)	$C_{26}H_{36}BNNaO_3$ (M+Na): 444.2686, found 444.2701 *m/z*

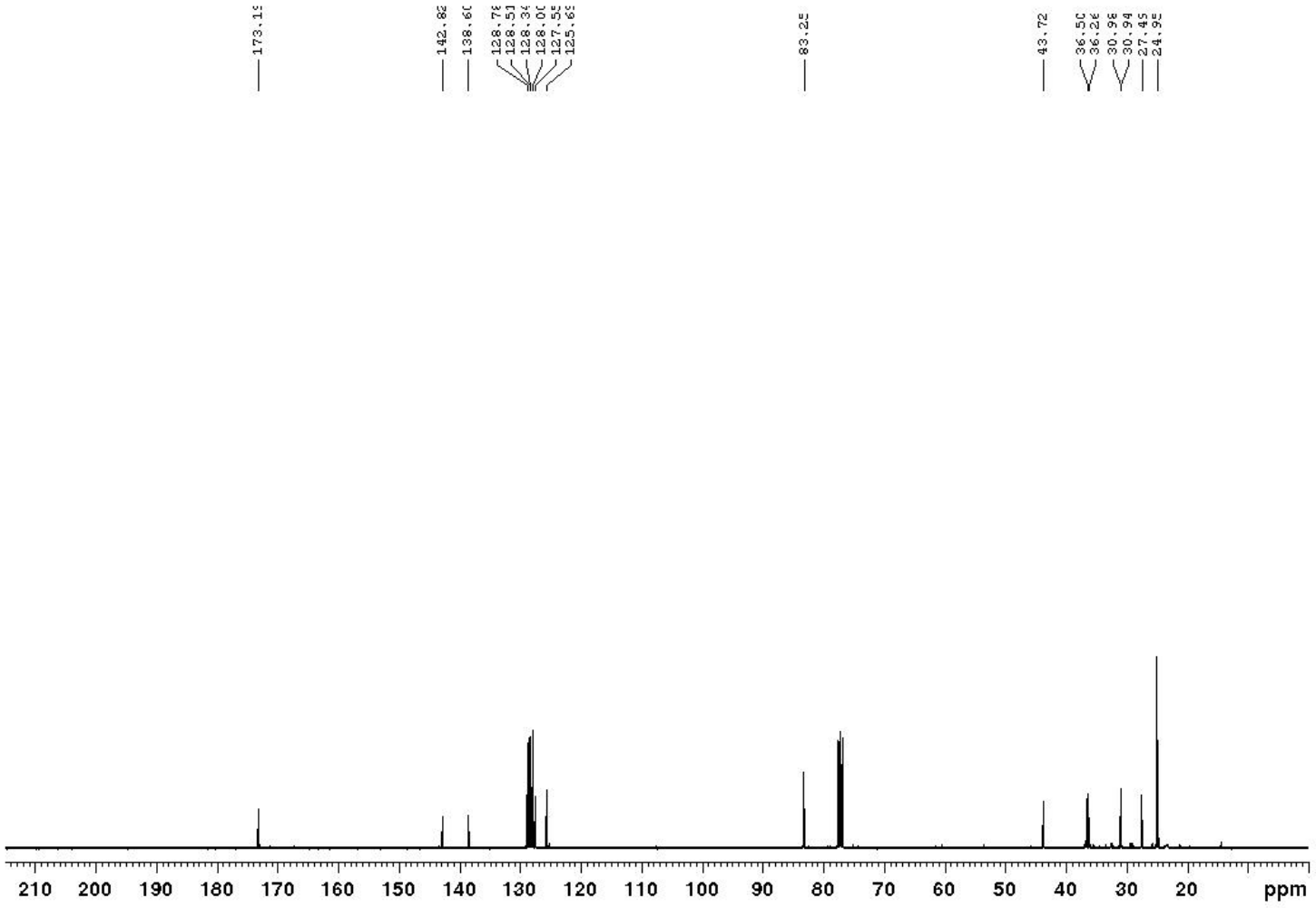
^{11}B NMR of 6d

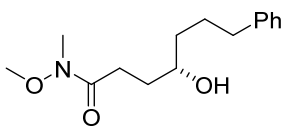


^{1}H NMR of 6d

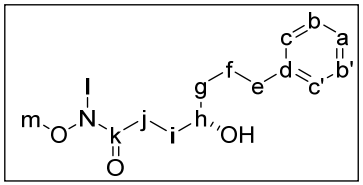

7.348
7.283
7.193
5.999
4.449
4.434
2.631
2.612
2.593
2.255
1.764
1.660
1.520
1.437
1.235
1.053
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.12
5.35
3.13
0.99
2.17
2.00
2.14
1.96
2.07
1.04
1.08
12.10
1.07

^{13}C NMR of 6d


173.1
142.8
138.6
128.7
128.5
128.3
128.0
127.5
125.6
83.2
43.7
36.5
36.2
30.9
30.9
27.4
24.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

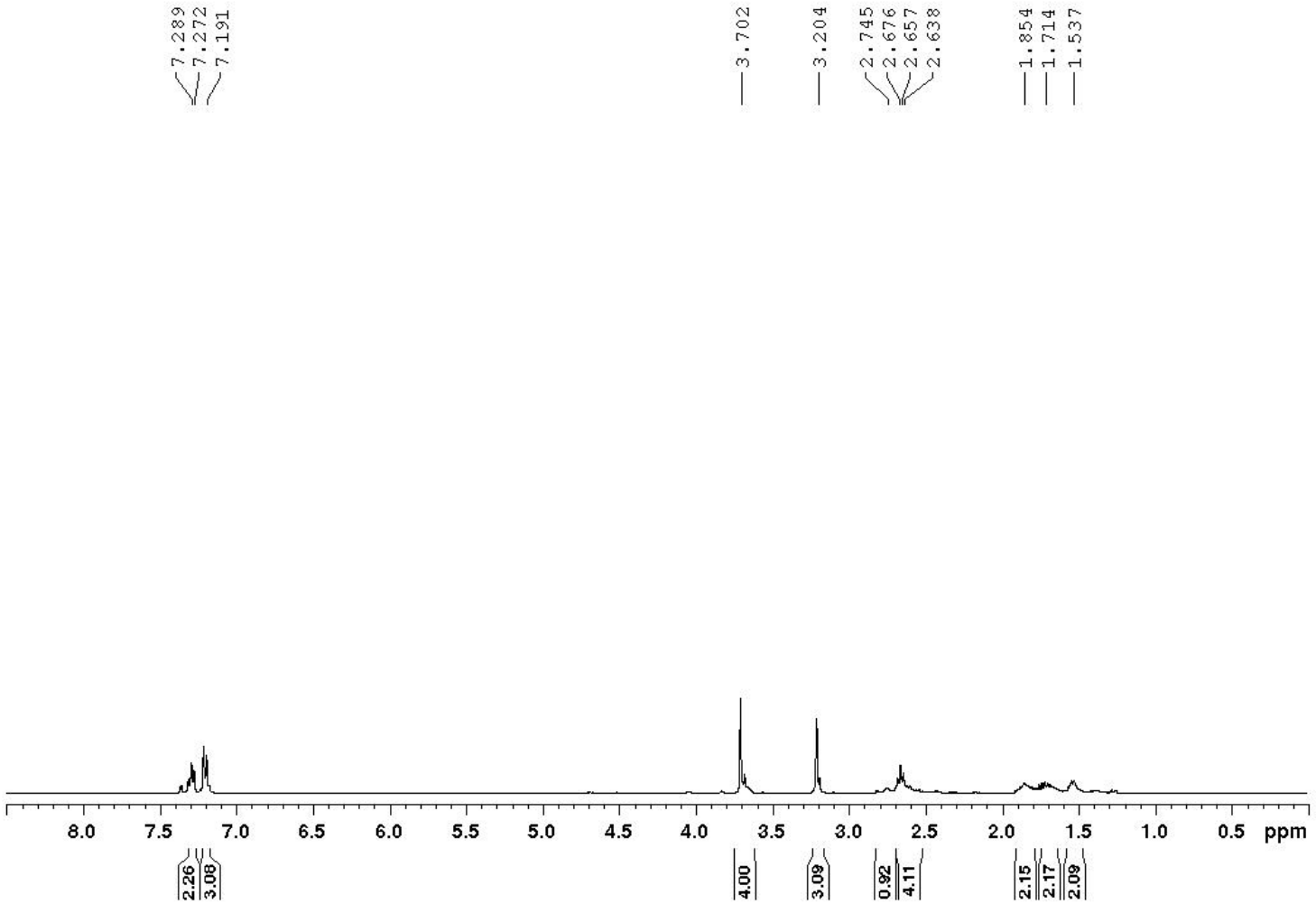


7b



$[\alpha]_D^{20}$	–12.5° (*c* 2.0, $CHCl_3$)
TLC analysis	R_f 0.5 (0:100 hexanes:ethyl acetate)
HPLC analysis	er of **7b** was determined by using harsh oxidation ($NaOH/H_2O_2$) instead of $NaBO_3$-tetrahydrate to form lactone **23** followed by transamidation with benzyl amine to generate **7d** (procedures described *vide infra*): Chiral HPLC analysis (Chiralpak-IC, 60:40 hexanes:isopropanol, flow rate = 1.3 mL/min) showed peaks at 26 minutes (4.0% (*R*)) and 30 minutes (96.0% (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.30 (2H, m, b,b'), 7.15–7.25 (3H, m, a,c,c'), 3.70 (3H, s, m), 3.60–3.70 (1H, m, h, *overlapping with* m), 3.20 (3H, s, l), 2.74 (1H, br s, OH), 2.66 (2H, t, *J* = 7.6 Hz, e), 2.50–2.70 (2H, m, j, *overlapping with* e), 1.80–1.90 (2H, m, f,i), 1.65–1.75 (2H, m, f,i), 1.45–1.65 (2H, m, g)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 175.19 (k), 142.55 (d), 128.54 (b,b'), 128.38 (c,c'), 125.78 (a), 71.45 (h), 61.35 (m), 37.36 (g), 35.99 (e), 32.37 (l), 31.74 (i), 28.63 (j), 27.62 (f)
IR (neat)	3430 (O-H stretch), 2933, 2858, 1639 (C=O stretch), 1452, 1416, 1386, 1177, 994, 748, 699 cm^{-1}
HRMS (ESI)	$C_{15}H_{23}NNaO_3$ (M+Na): 288.1576, found 288.1583 *m/z*

^{1}H NMR of 7b


7.289
7.272
7.191
3.702
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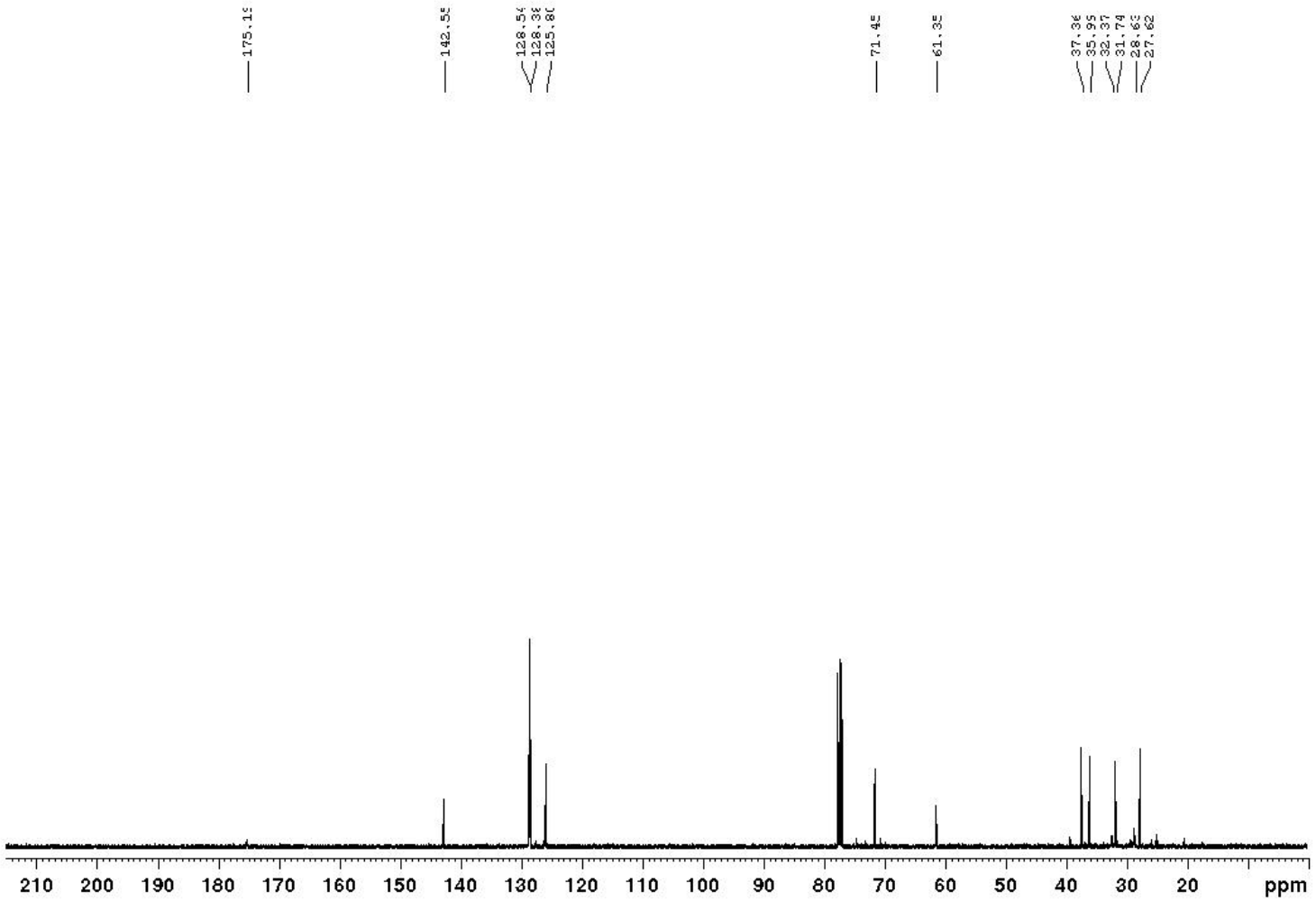
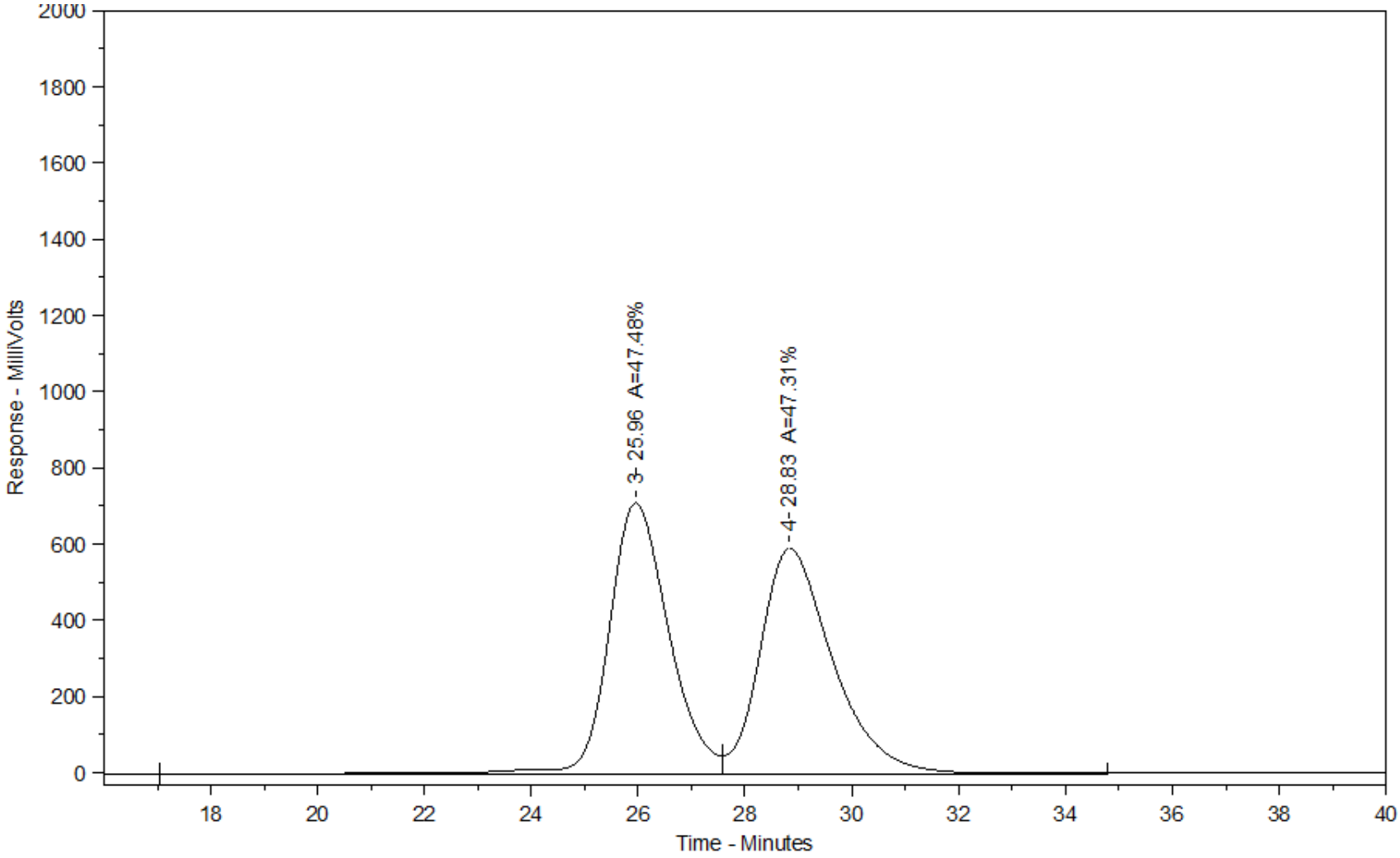
2.745
2.676
2.657
2.638
1.854
1.714
1.537
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.26
3.08
4.00
3.09
0.92
4.11
2.15
2.17
2.09

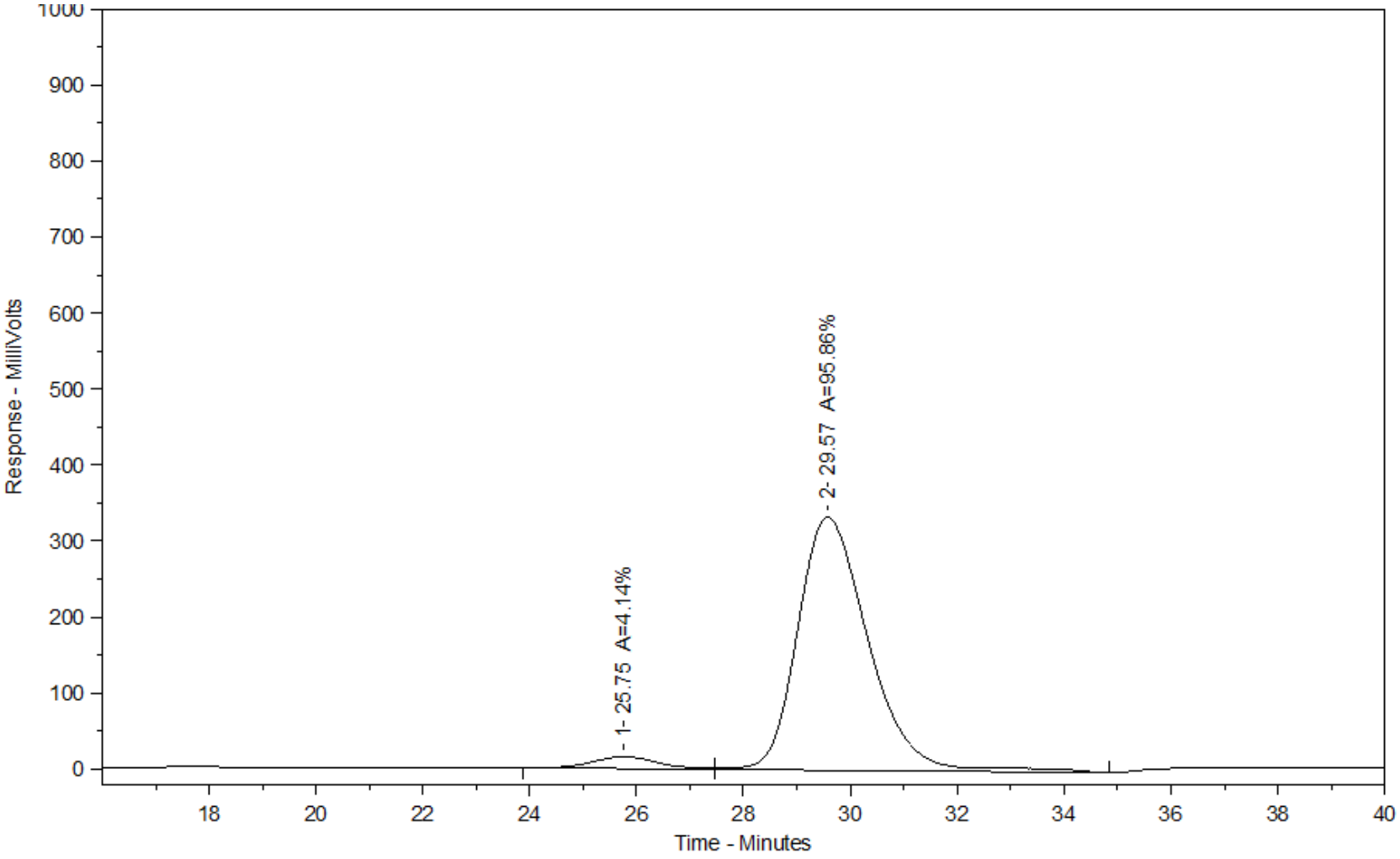
^{13}C NMR of 7b


175.1
142.5
128.5
128.3
125.8
71.4
61.3
37.3
35.9
32.3
31.7
28.6
27.6
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

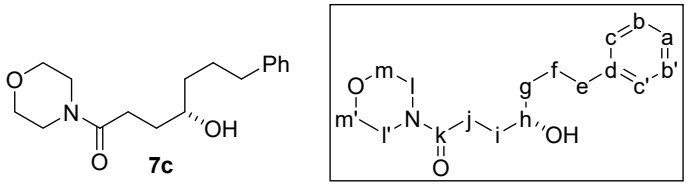
HPLC trace of 7d from CAHB of 5b



Racmic **7d**

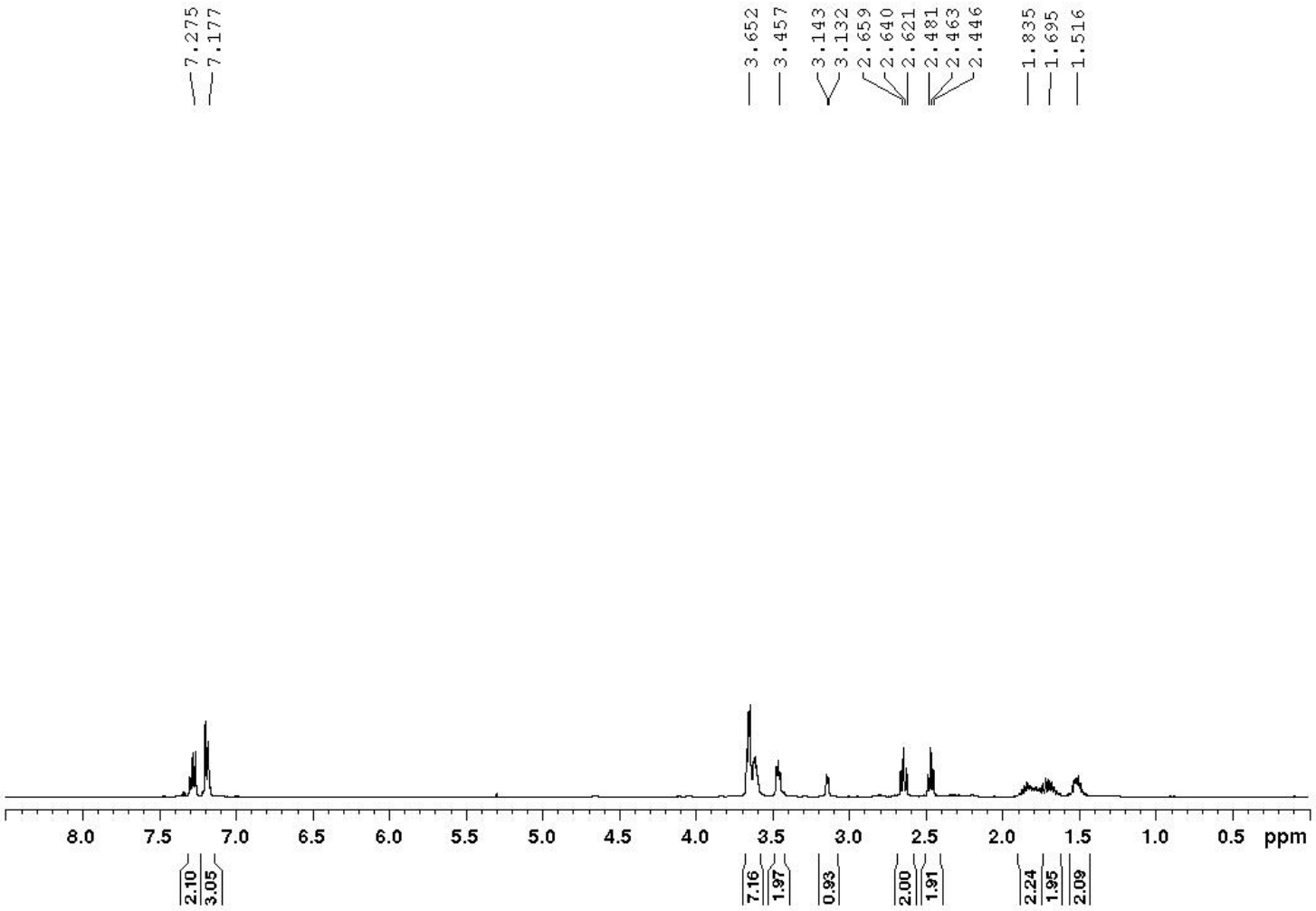


(*S*)-**7d** (from CAHB of **5b**)



$[\alpha]_D^{20}$	–5.1° (*c* 2.0, $CHCl_3$)
TLC analysis	R_f 0.7 (20:80 hexanes:acetone)
HPLC analysis	er of **7c** was determined by boric acid-catalyzed transamidation with benzyl amine to form **7d**: Chiral HPLC analysis (Chiralpak-IC, 60:40 hexanes:isopropanol, flow rate = 1.3 mL/min) showed peaks at 28 minutes (5.5 0% (*R*)) and 31 minutes (94.5% (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.30 (2H, m, b,b'), 7.15–7.20 (3H, m, a,c,c'), 3.55–3.70 (7H, m, h,l,l',m,m'), 3.40–3.50 (2H, m, l,l'), 2.64 (2H, t, *J* = 7.6 Hz, e), 2.46 (2H, t, *J* = 7.0 Hz, j), 1.75–1.90 (2H, m, f,i), 1.60–1.75 (2H, m, f,i), 1.45–1.60 (2H, m, g)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.44 (k), 142.50 (d), 128.53 (b,b'), 128.39 (c,c'), 125.83 (a), 71.28 (h), 66.95 and 66.68 (m,m'), 46.11 and 42.14 (l,l'), 37.44 (g), 35.97 (e), 32.11 (i), 29.75 (j), 27.62 (f)
IR (neat)	3418 (O-H stretch), 2919, 2855, 1622 (C=O stretch), 1432, 1271, 1232, 1114, 1068, 1031, 748, 699 cm^{-1}
HRMS (ESI)	$C_{17}H_{25}NNaO_3$ (M+Na): 314.1732, found 314.1743 *m/z*

^{1}H NMR of 7c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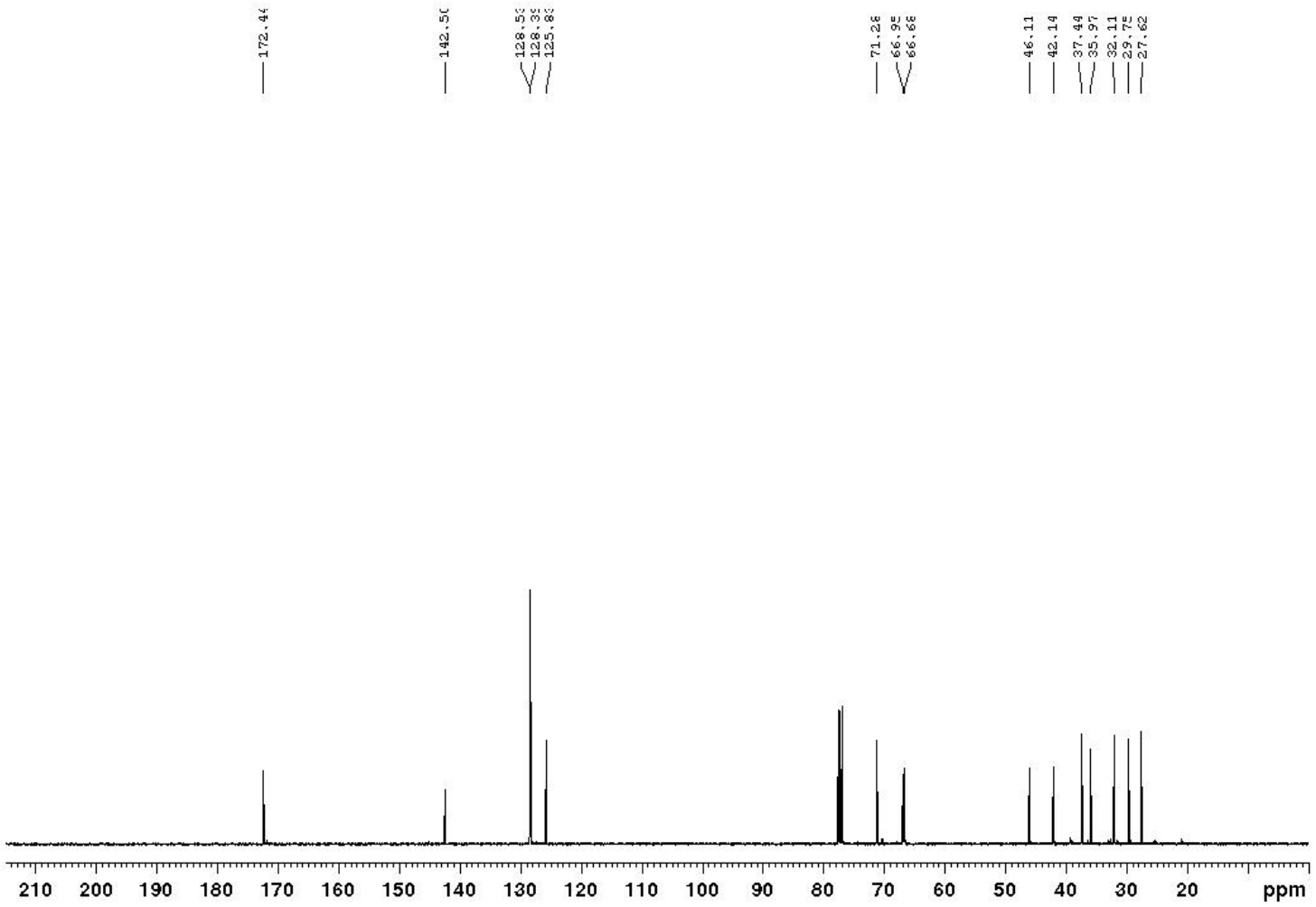
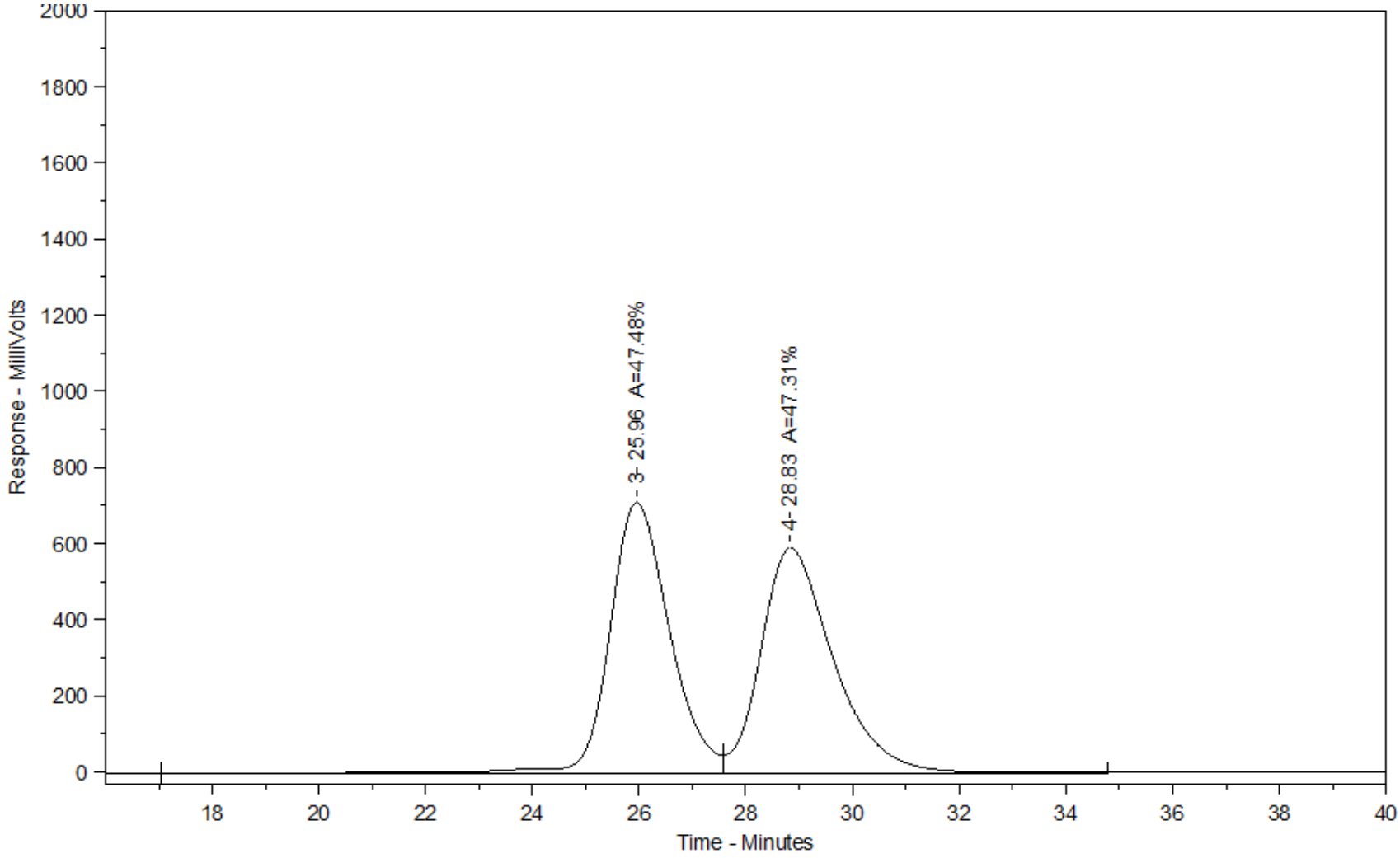
3.457
3.143
3.132
2.659
2.640
2.621
2.481
2.463
2.446
1.835
1.695
1.516
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.10
3.05
7.16
1.97
0.93
2.00
1.91
2.24
1.95
2.09

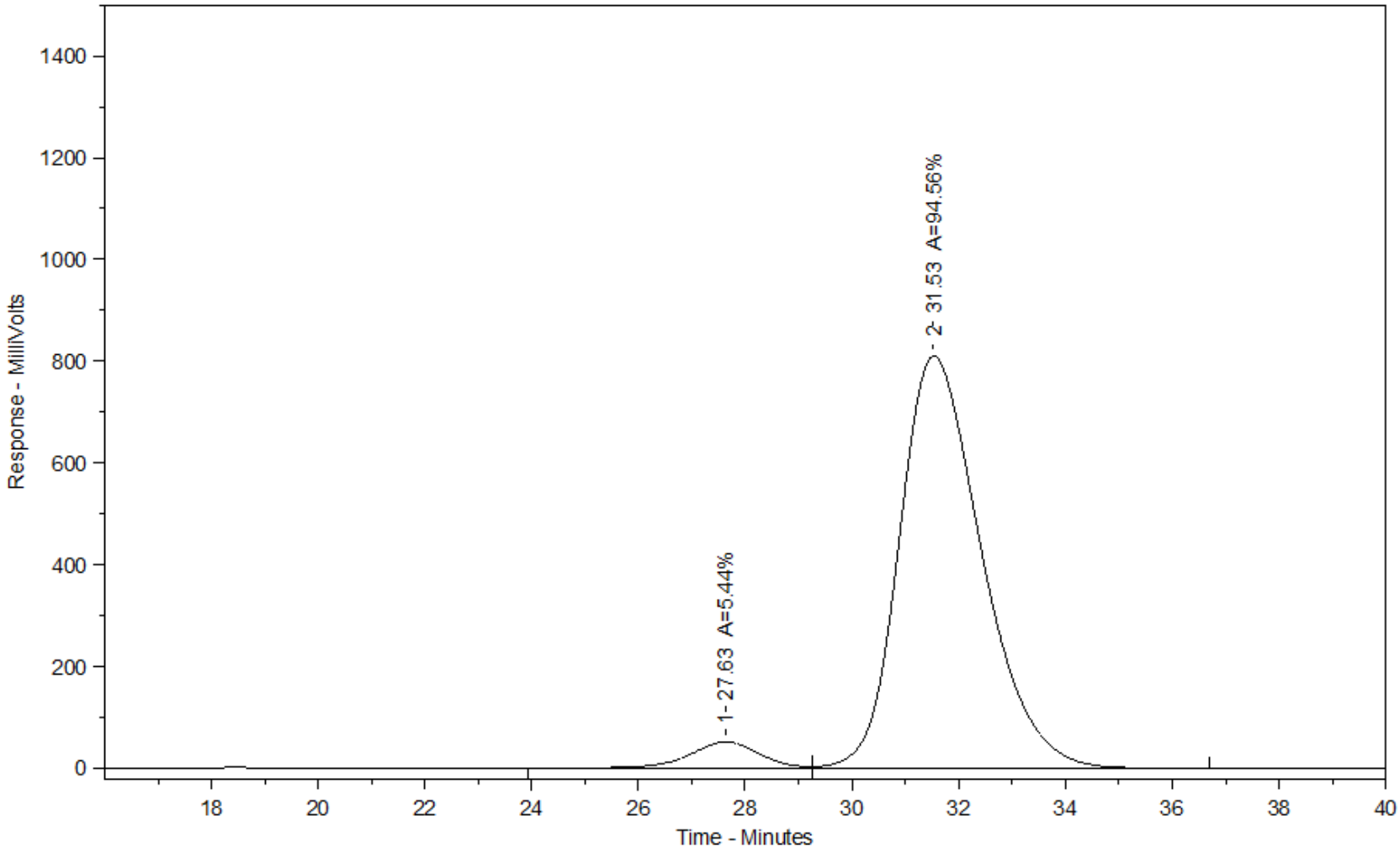
^{13}C NMR of 7c


172.44
142.50
128.53
128.38
125.83
71.26
66.95
66.68
46.11
42.14
37.49
35.97
32.11
29.75
27.62
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

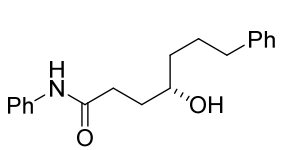
HPLC trace of 7d from CAHB of 5c



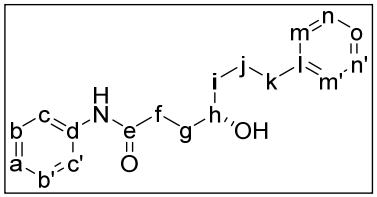
Racmic **7d**



(*S*)-**7d** (from CAHB of **5c**)

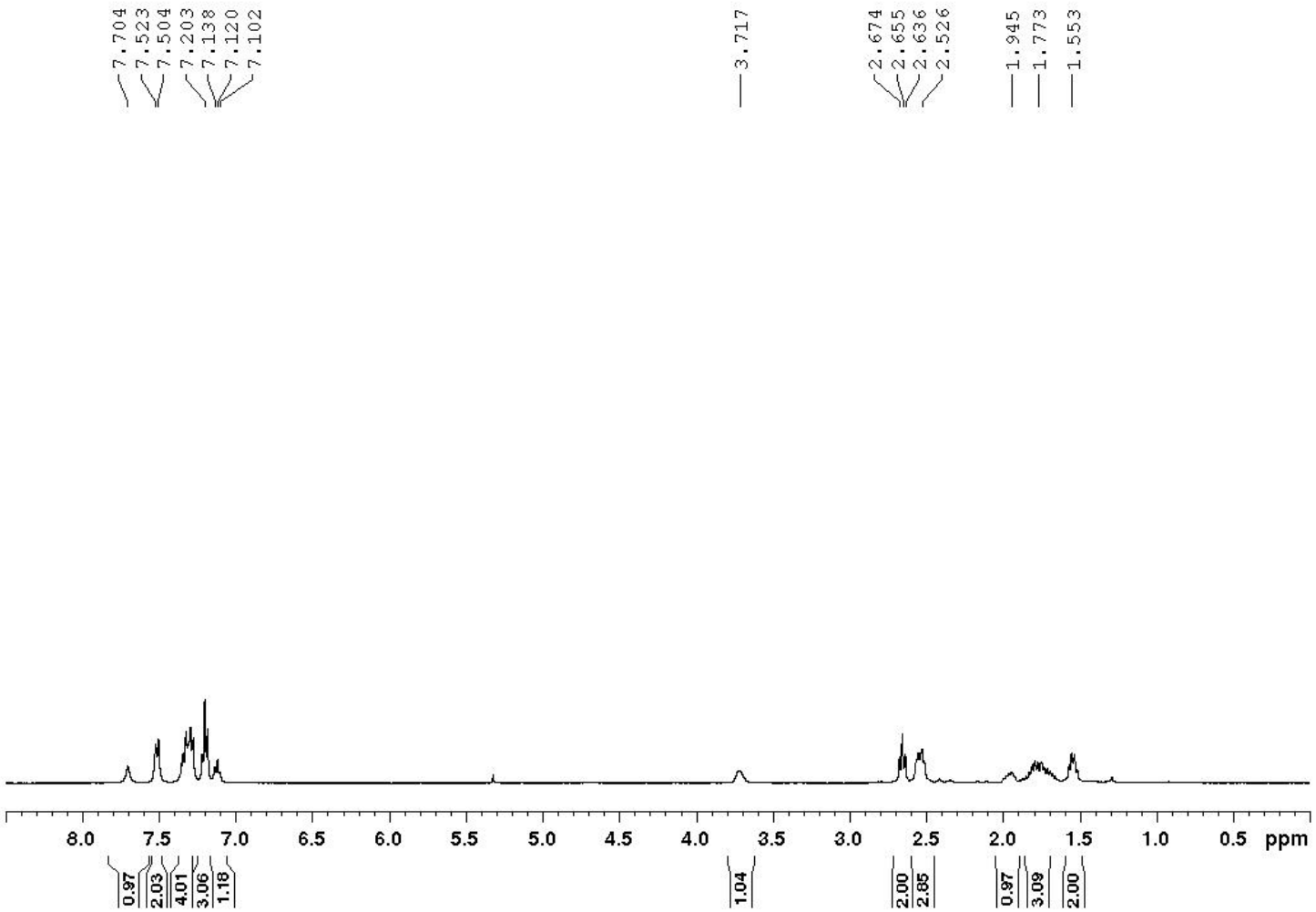


7a

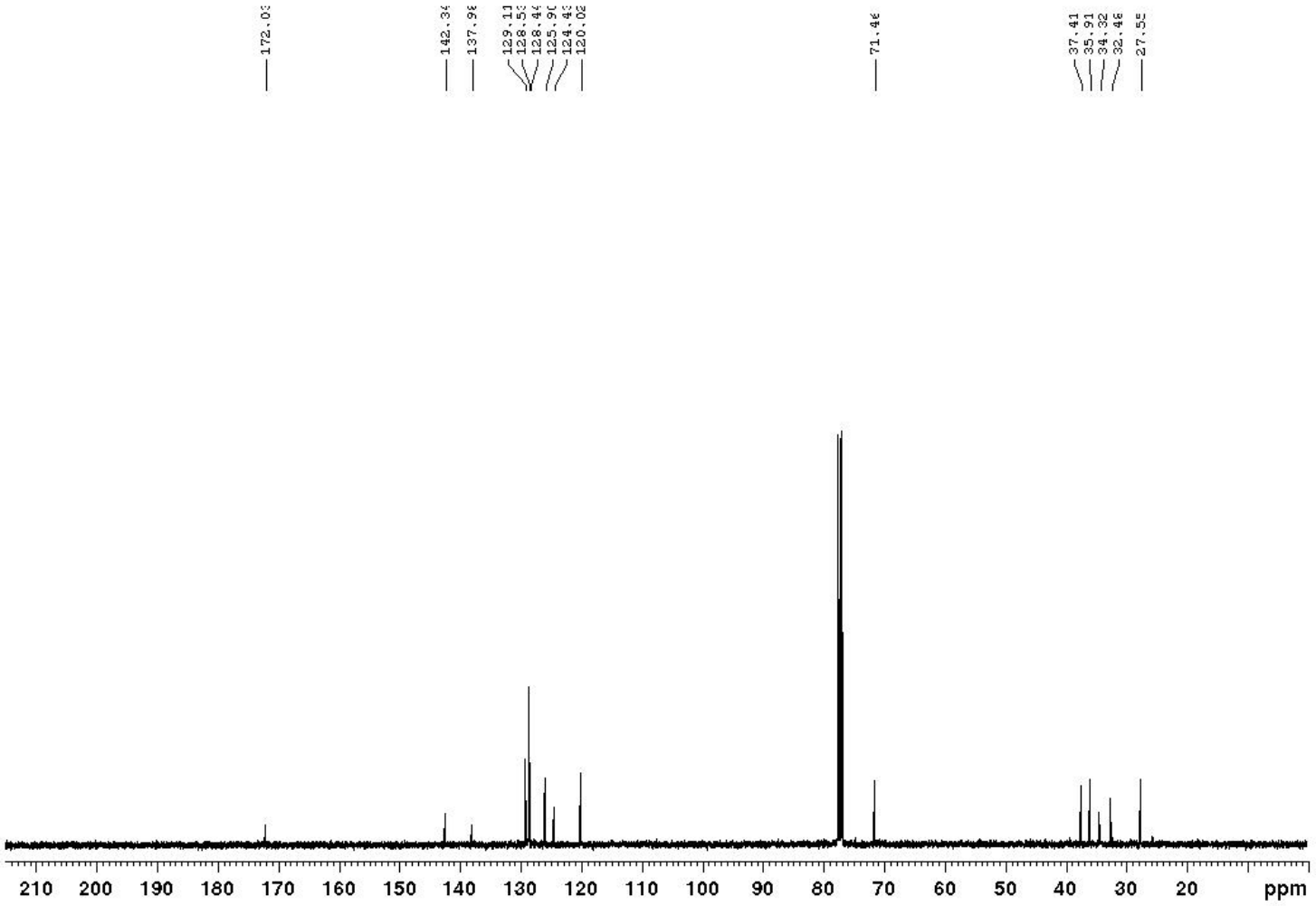


$[\alpha]_D^{20}$	+7.5º (*c* 1.0, MeOH)
m.p.	119.5–120.5 ºC
TLC analysis	R_f 0.3 (40:60 hexanes:ethyl acetate)
HPLC analysis	Chiral HPLC analysis (Chiralpak-IB, 70:30 hexanes:isopropanol, flow rate = 1.4 mL/min) showed peaks at 41 minutes (3.0% (*R*)) and 44 minutes (97.0% (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.70 (1H, br s, NH), 7.51 (2H, d, *J* = 7.7 Hz, c,c'), 7.25–7.35 (4H, m, b,b',m,m'), 7.15–7.25 (3H, m, b,b',n,n',o), 7.12 (1H, t, *J* = 7.3 Hz, a), 3.60–3.80 (1H, m, h), 2.65 (2H, t, *J* = 7.8 Hz, k), 2.45–2.60 (3H, m, f, OH), 1.90–2.00 (1H, m, g), 1.70–1.85 (3H, m, g,j), 1.50–1.60 (2H, m, i)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.03 (e), 142.34 (l), 137.98 (d), 129.11 (b,b'), 128.53 (n,n'), 128.44 (m,m'), 125.90 (o), 124.43 (a), 120.02 (c,c'), 71.46 (h), 37.41 (i), 35.91 (k), 34.32 (f), 32.48 (g), 27.55 (j)
IR (neat)	3670 (N-H stretch, O-H stretch), 3279, 3247, 2950, 2911, 1659 (C=O stretch), 1600 (N-H bend), 1543, 1496, 1412 (C-N stretch), 754, 689 cm^{-1}
HRMS (ESI)	$C_{19}H_{23}NNaO_2$ (M+Na): 320.1626, found 320.1631 *m/z*

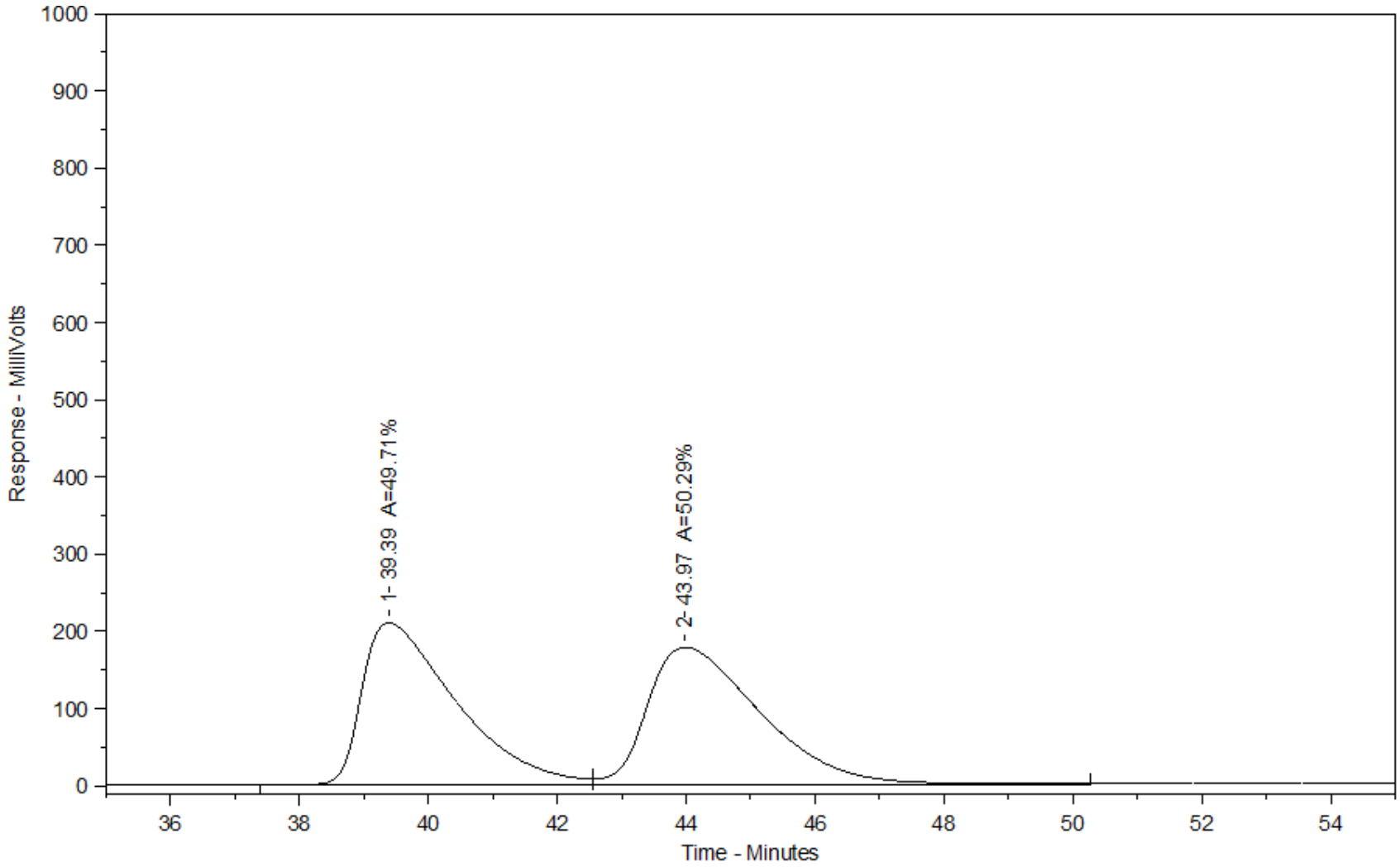
^{1}H NMR of 7a


7.704
7.523
7.504
7.203
7.138
7.120
7.102
3.717
2.674
2.655
2.636
2.526
1.945
1.773
1.553
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.97
2.03
4.01
3.06
1.18
1.04
2.00
2.85
0.97
3.09
2.00

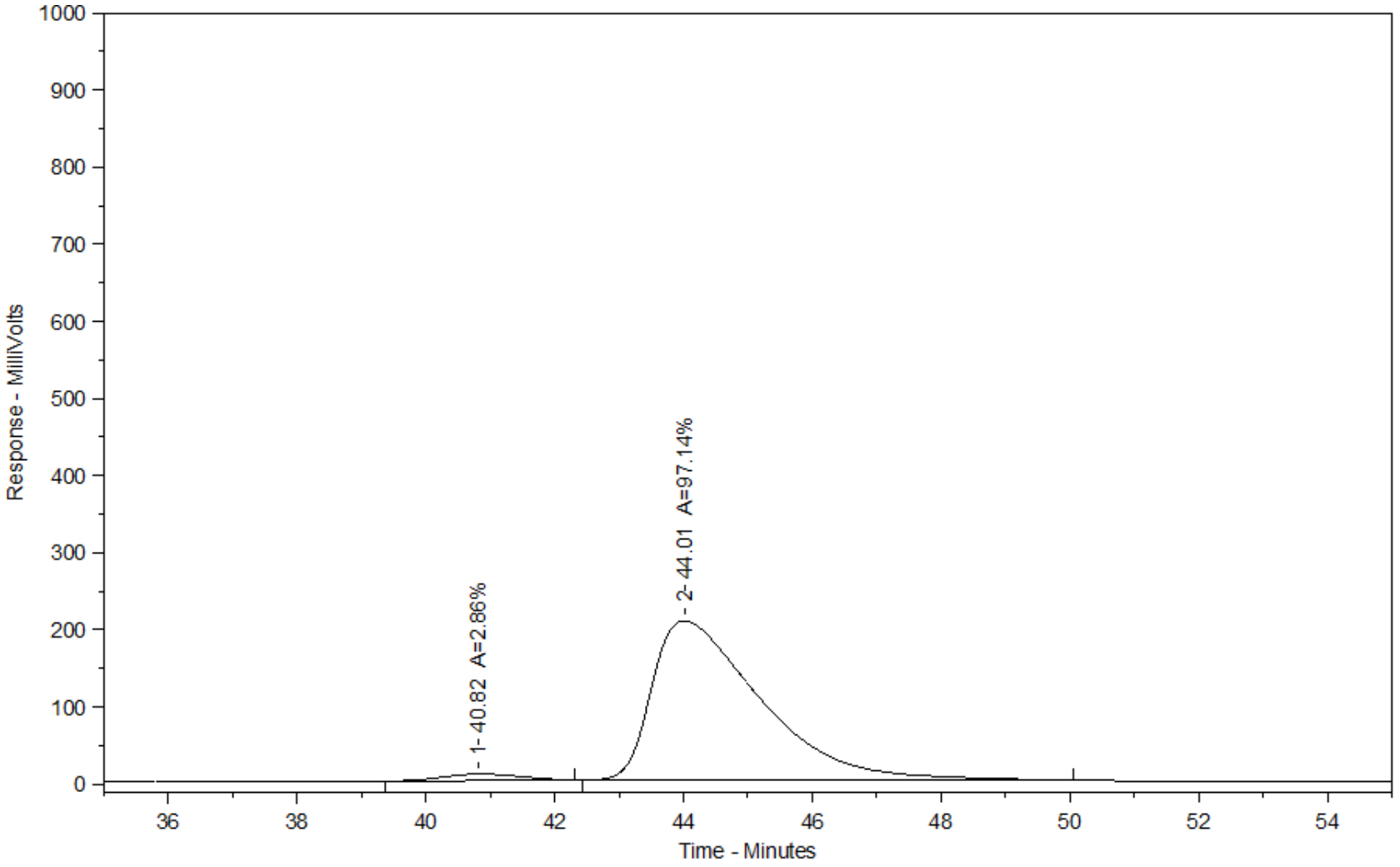
^{13}C NMR of 7a


172.03
142.34
137.98
129.11
128.55
128.44
125.90
124.43
120.02
71.46
37.41
35.91
34.32
32.46
27.55
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

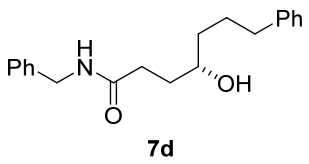
HPLC trace of 7a



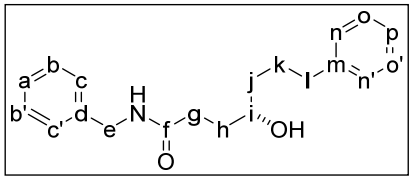
Racemic **7a**


1000
900
800
700
600
500
400
300
200
100
0
Response - MilliVolts
1- 40.82 A=2.86%
2- 44.01 A=97.14%
36
38
40
42
44
46
48
50
52
54
Time - Minutes

(*S*)-**7a**

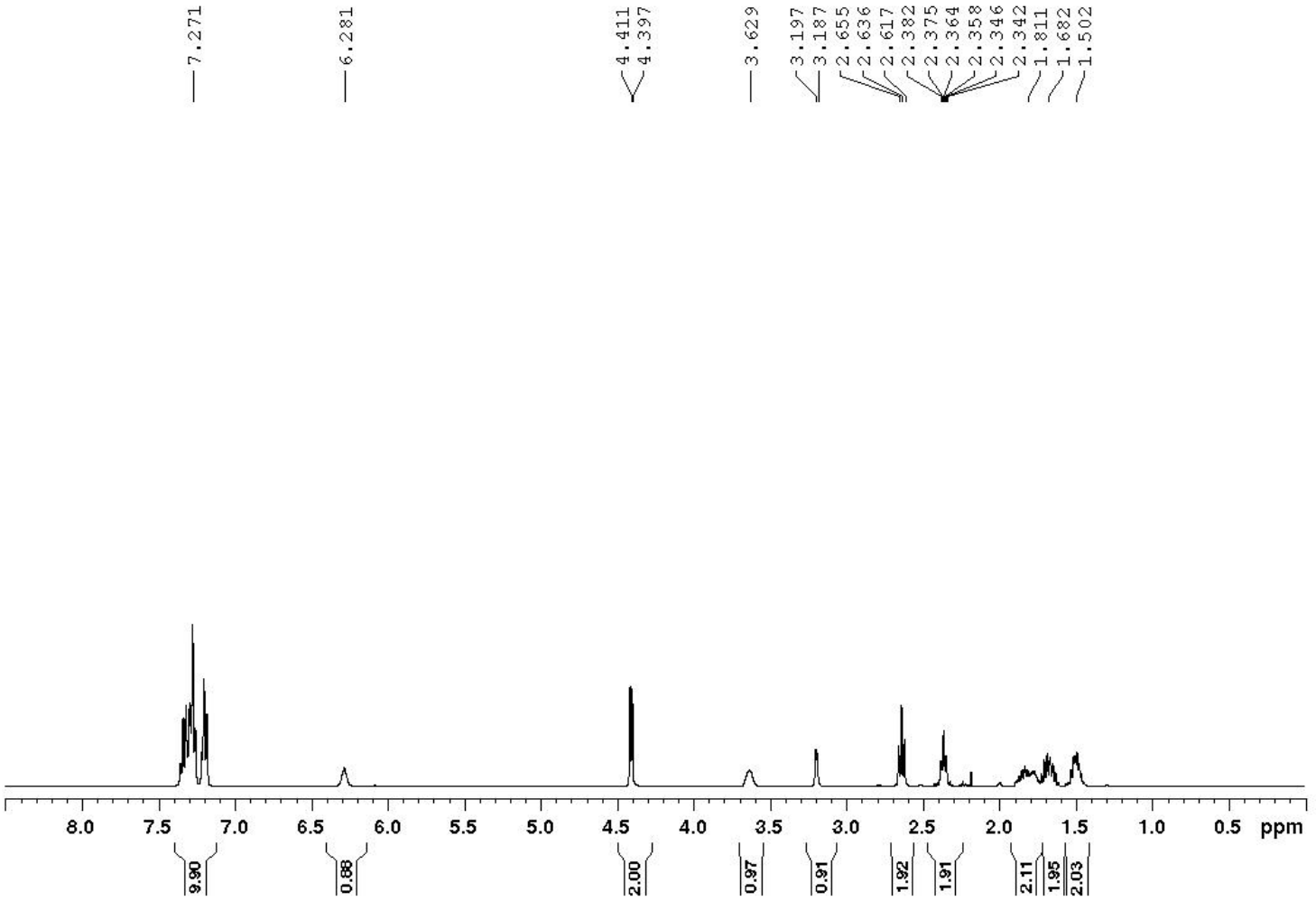


7d

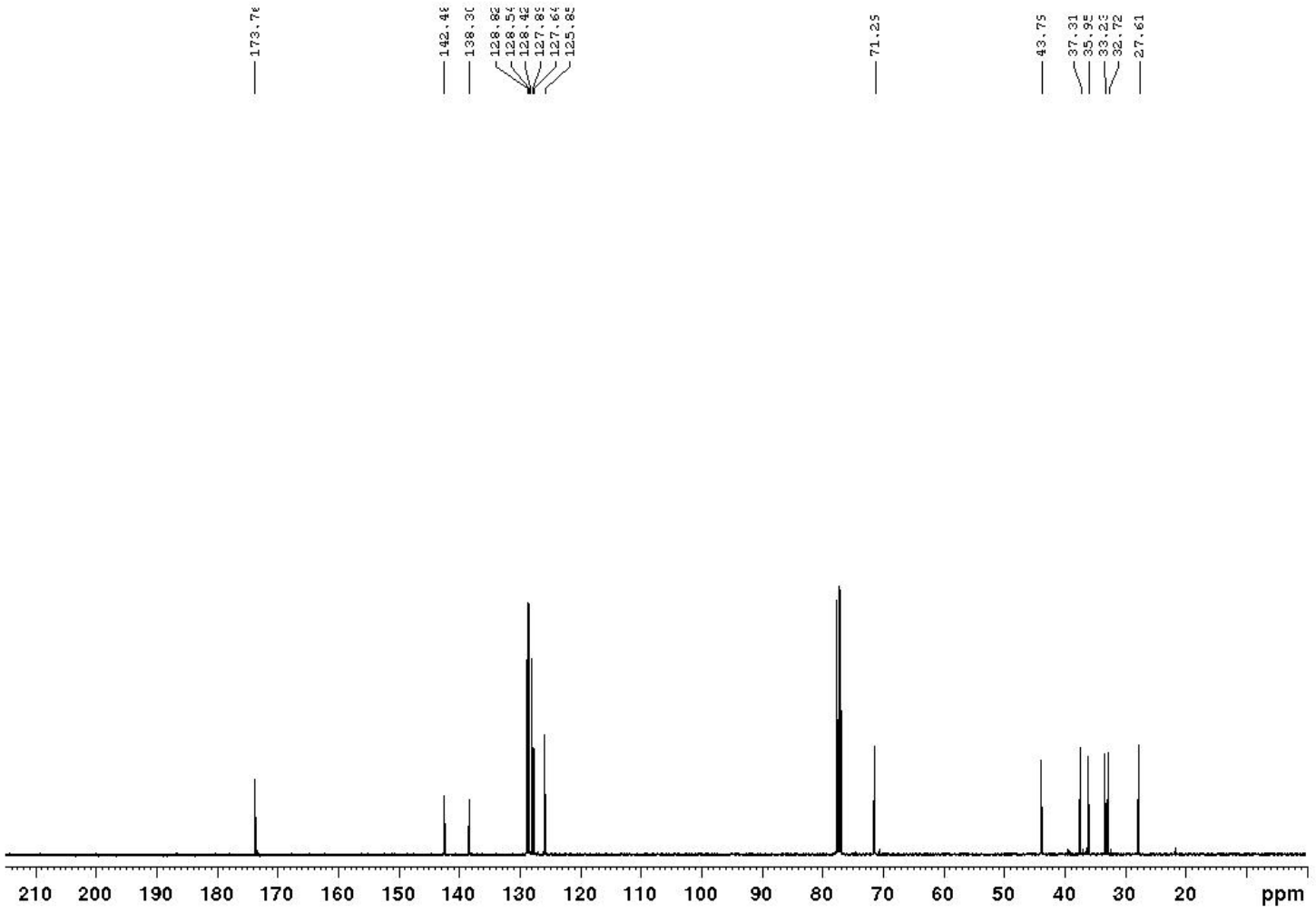


$[\alpha]_D^{20}$	–7.9º (*c* 1.0, $CHCl_3$)
m.p.	88.5–89.5 ºC
TLC analysis	R_f 0.4 (0:100 hexanes:ethyl acetate)
HPLC analysis	Chiral HPLC analysis (Chiralpak-IC, 60:40 hexanes:isopropanol, flow rate = 1.3 mL/min) showed peaks at 28 minutes (3.5% (*R*)) and 32 minutes (96.5% (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.10–7.40 (10H, a,b,b',c,c',n,n',o,o',p), 6.28 (1H, br s, NH), 4.40 (2H, d, *J* = 5.7 Hz, e), 3.55–3.70 (1H, m, i), 3.19 (1H, d, *J* = 4.2 Hz, OH), 2.64 (2H, t, *J* = 7.6 Hz, l), 2.36 (2H, td, *J* = 7.3 and 2.8 Hz, g), 1.70–1.90 (2H, m, h,k), 1.60–1.70 (2H, m, h,k), 1.40–1.60 (2H, m, j)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.76 (f), 142.48 (m), 138.30 (d), 128.82 (b,b'), 128.54 (o,o'), 128.42 (n,n'), 127.89 (c,c'), 127.64 (a), 125.85 (p), 71.29 (i), 43.79 (e), 37.31 (j), 35.95 (l), 33.23 (g), 32.72 (h), 27.61 (k)
IR (neat)	3306 (N-H stretch, O-H stretch), 3025, 2937, 2919, 2867, 1637 (C=O stretch), 1546 (N-H bend), 1495, 1442, 1234, 724, 694 cm^{-1}
HRMS (ESI)	$C_{20}H_{25}NNaO_2$ (M+Na): 334.1783, found 334.1781 *m/z*

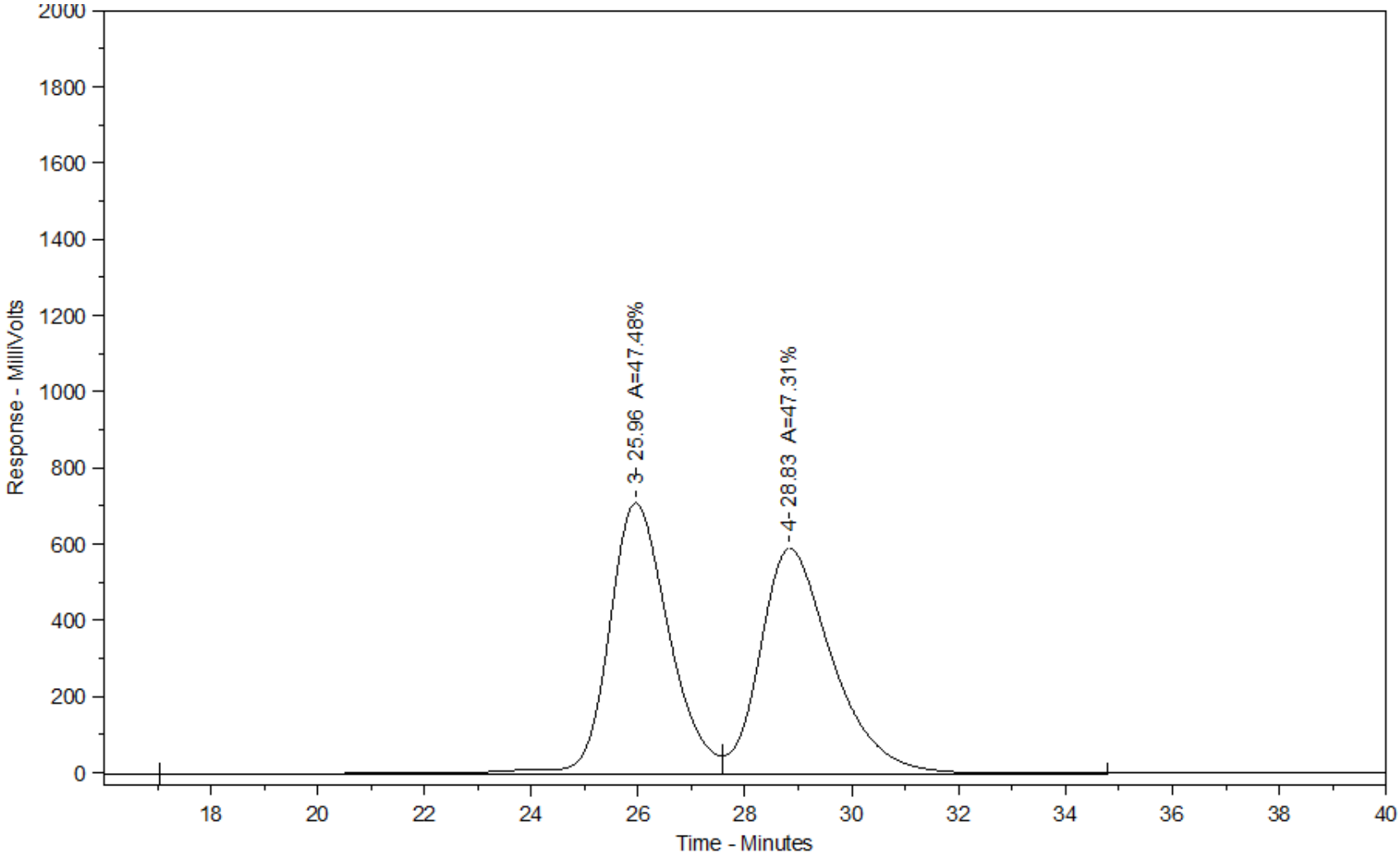
^{1}H NMR of 7d


7.271
6.281
4.411
4.397
3.629
3.197
3.187
2.655
2.636
2.617
2.382
2.375
2.364
2.358
2.346
2.342
1.811
1.682
1.502
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
9.90
0.88
2.00
0.97
0.91
1.92
1.91
2.11
1.95
2.03

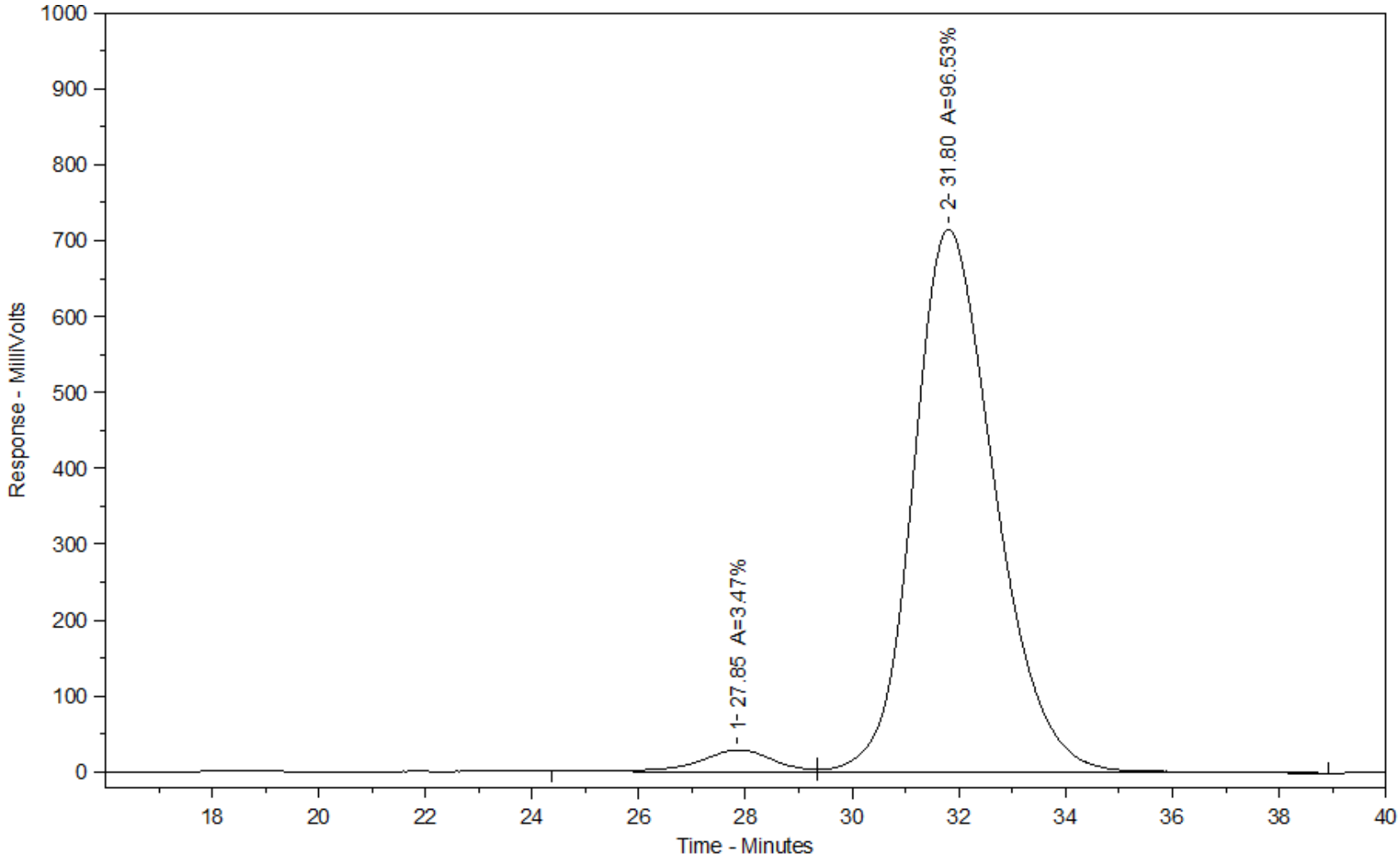
^{13}C NMR of 7d


173.7
142.4
138.3
128.8
128.5
128.4
127.8
127.6
125.8
71.25
43.75
37.31
35.9
33.2
32.72
27.61
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

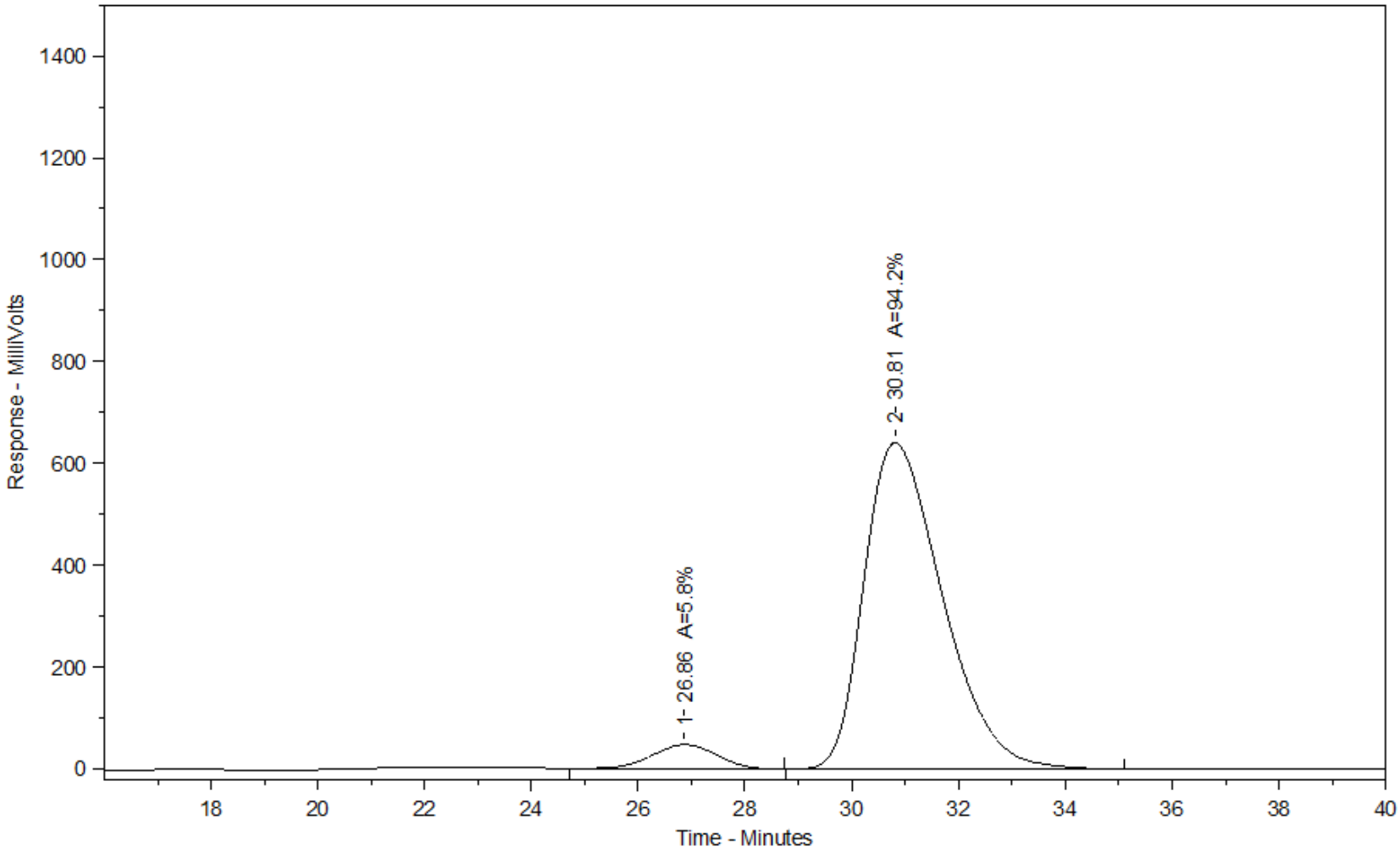
HPLC trace of 7d



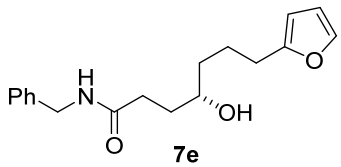
Racmic **7d**

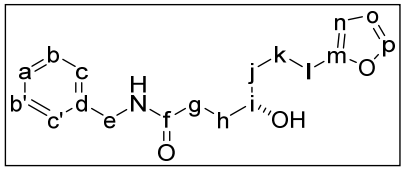


(*S*)-**7d** (from CAHB of (*E*)-**5d**)



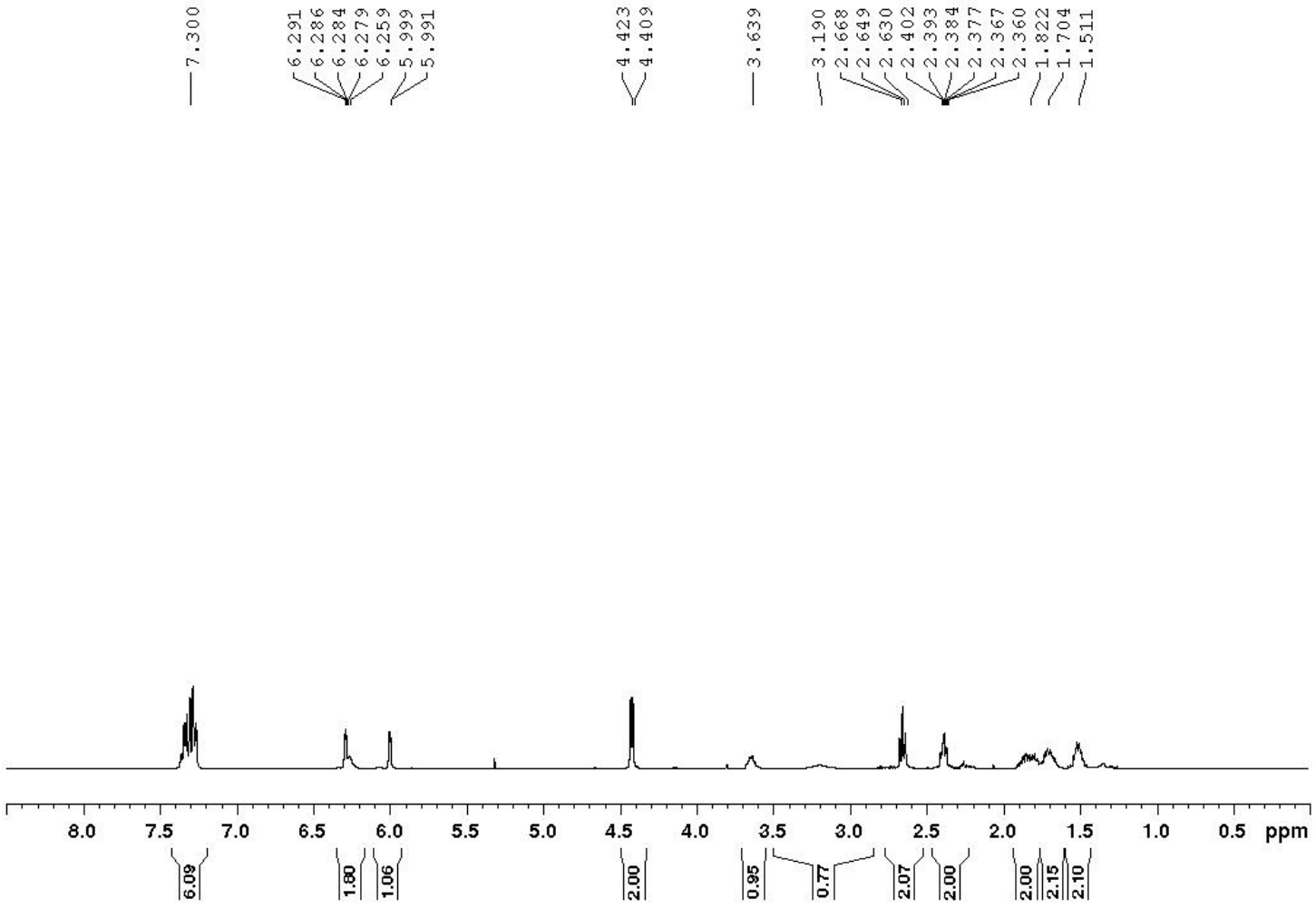
(*S*)-**7d** (from CAHB of (*Z*)-**5d**)



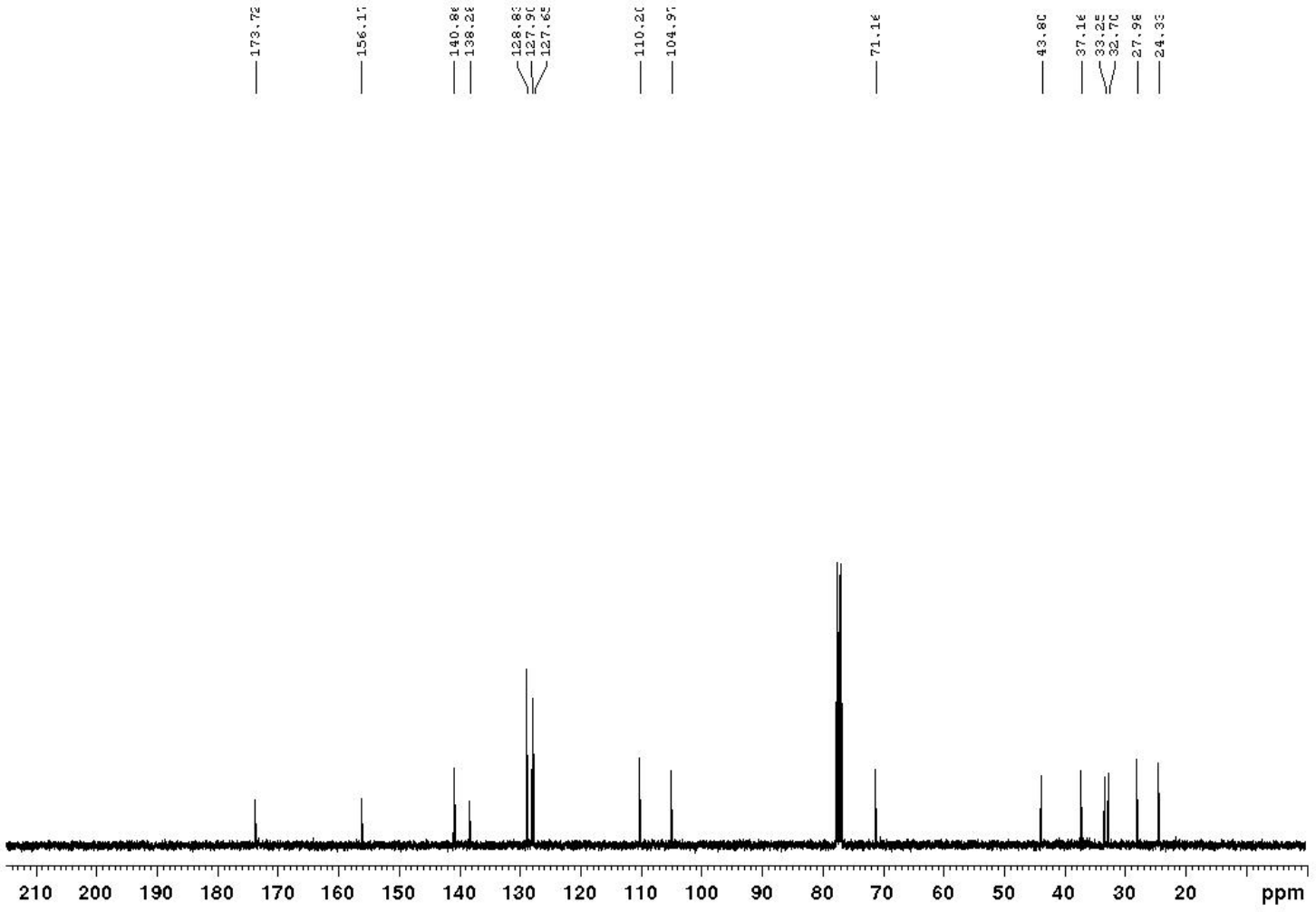


$[\alpha]_D^{20}$	–6.1° (*c* 2.0, $CHCl_3$)
m.p.	72.5–74.0 ºC
TLC analysis	R_f 0.35 (0:100 hexanes:ethyl acetate)
HPLC analysis	Chiral HPLC analysis (Chiralpak-IB, 60:40 hexanes:isopropanol, flowrate = 1.4 mL/min) showed peaks at 18 minutes (94.0% (*S*)) and 47 minutes (6.0% (*R*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.20–7.40 (6H, a,b,b',c,c',p), 6.29 (1H, dd, *J* = 2.9 and 2.0 Hz, o), 6.26 (1H, br s, NH, *overlapping with* o), 6.00 (1H, d, *J* = 3.0 Hz, n), 4.42 (2H, d, *J* = 5.7 Hz, e), 3.55–3.70 (1H, m, i), 2.85–3.45 (1H, br s, OH), 2.65 (2H, t, *J* = 7.4 Hz, l), 2.38 (2H, td, *J* = 7.2 and 3.4 Hz, g), 1.75–1.90 (2H, m, h,k), 1.60–1.75 (2H, m, h,k), 1.40–1.60 (2H, m, j)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.72 (f), 156.17 (m), 140.86 (p), 138.28 (d), 128.83 (b,b'), 127.90 (c,c'), 127.65 (a), 110.20 (o), 104.97 (n), 71.16 (i), 43.80 (e), 43.79 (e), 37.16 (j), 33.25 (g), 32.70 (h), 27.98 (l), 24.33 (k)
IR (neat)	3288 (N-H stretch, O-H stretch), 2919, 1632 (C=O stretch), 1534, 1453, 1090, 1006, 723, 695 cm^{-1}
HRMS (ESI)	$C_{18}H_{23}NNaO_3$ (M+Na): 324.1576, found 324.1573 *m/z*

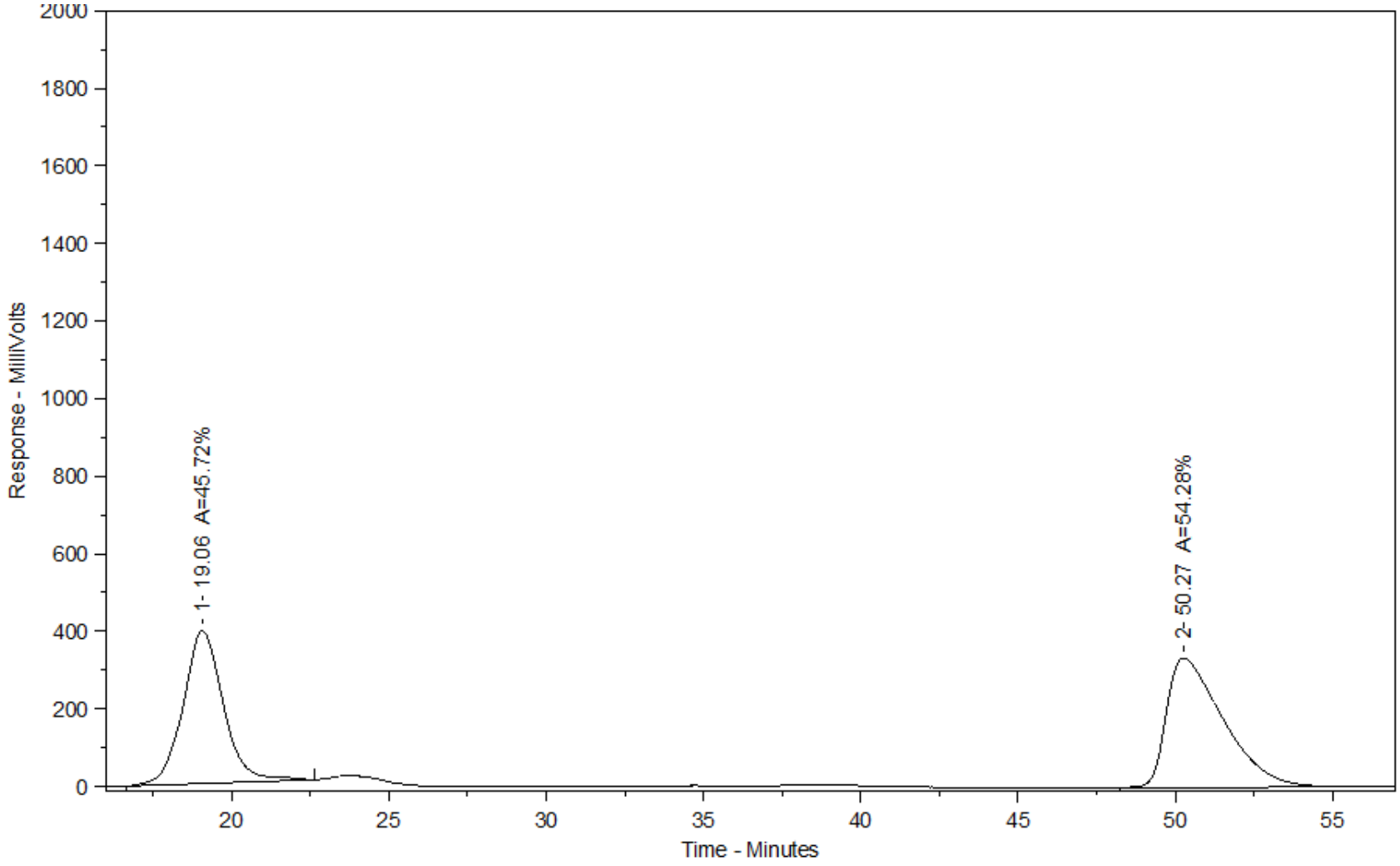
^{1}H NMR of 7e


7.300
6.291
6.286
6.284
6.279
6.259
5.999
5.991
4.423
4.409
3.639
3.190
2.668
2.649
2.630
2.402
2.393
2.384
2.377
2.367
2.360
1.822
1.704
1.511
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
6.09
1.80
1.06
2.00
0.95
0.77
2.07
2.00
2.00
2.15
2.10

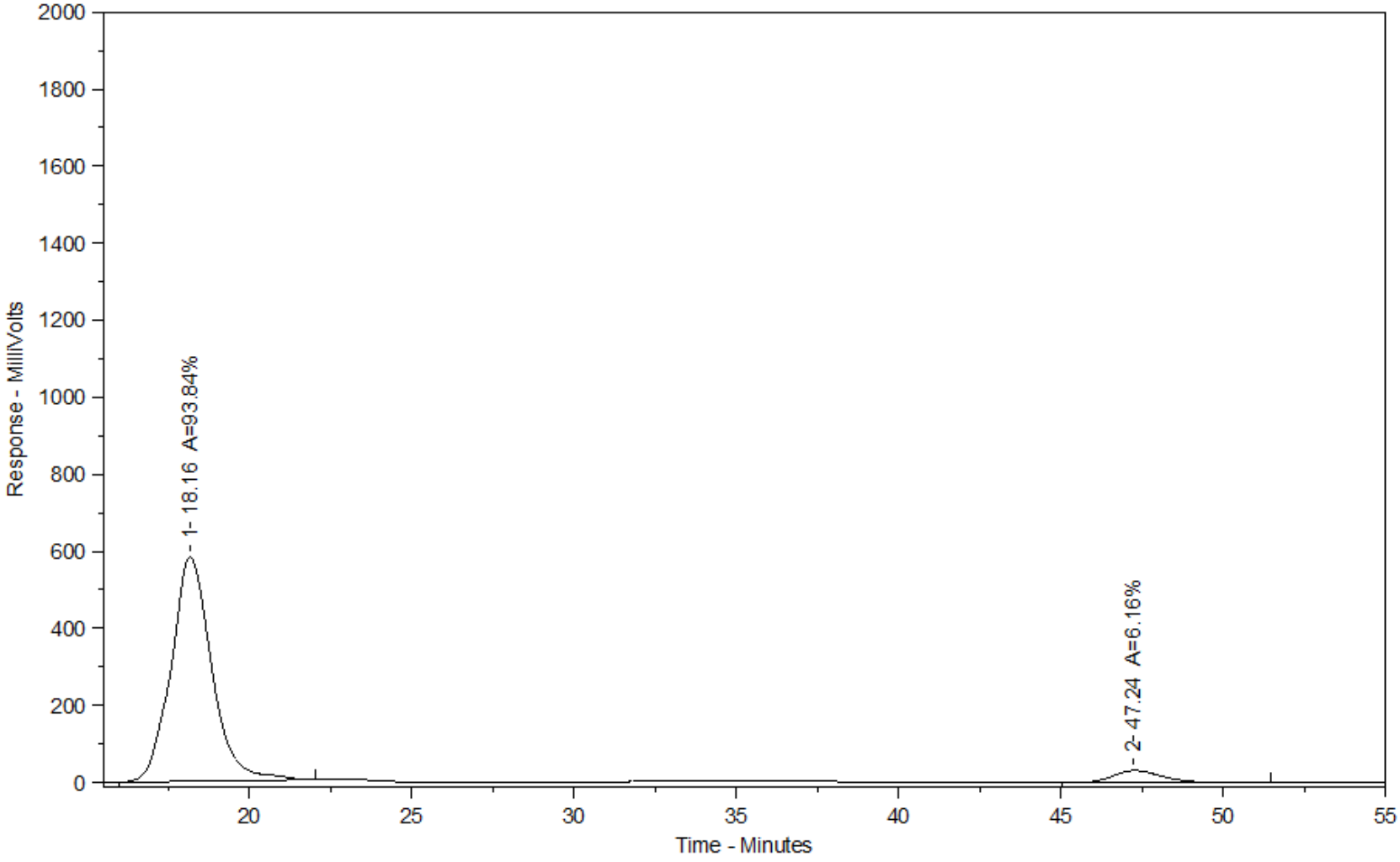
^{13}C NMR of 7e


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

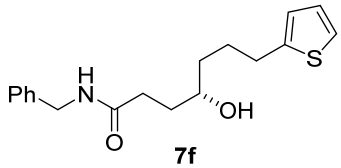
HPLC trace of 7e



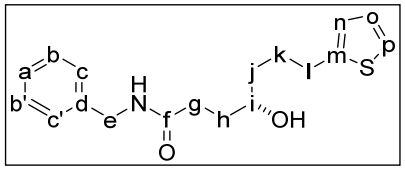
Racemic **7e**


Response - MilliVolts
Time - Minutes
1- 18.16 A=93.84%
2- 47.24 A=6.16%
0
200
400
600
800
1000
1200
1400
1600
1800
2000
20
25
30
35
40
45
50
55

(*S*)-**7e**

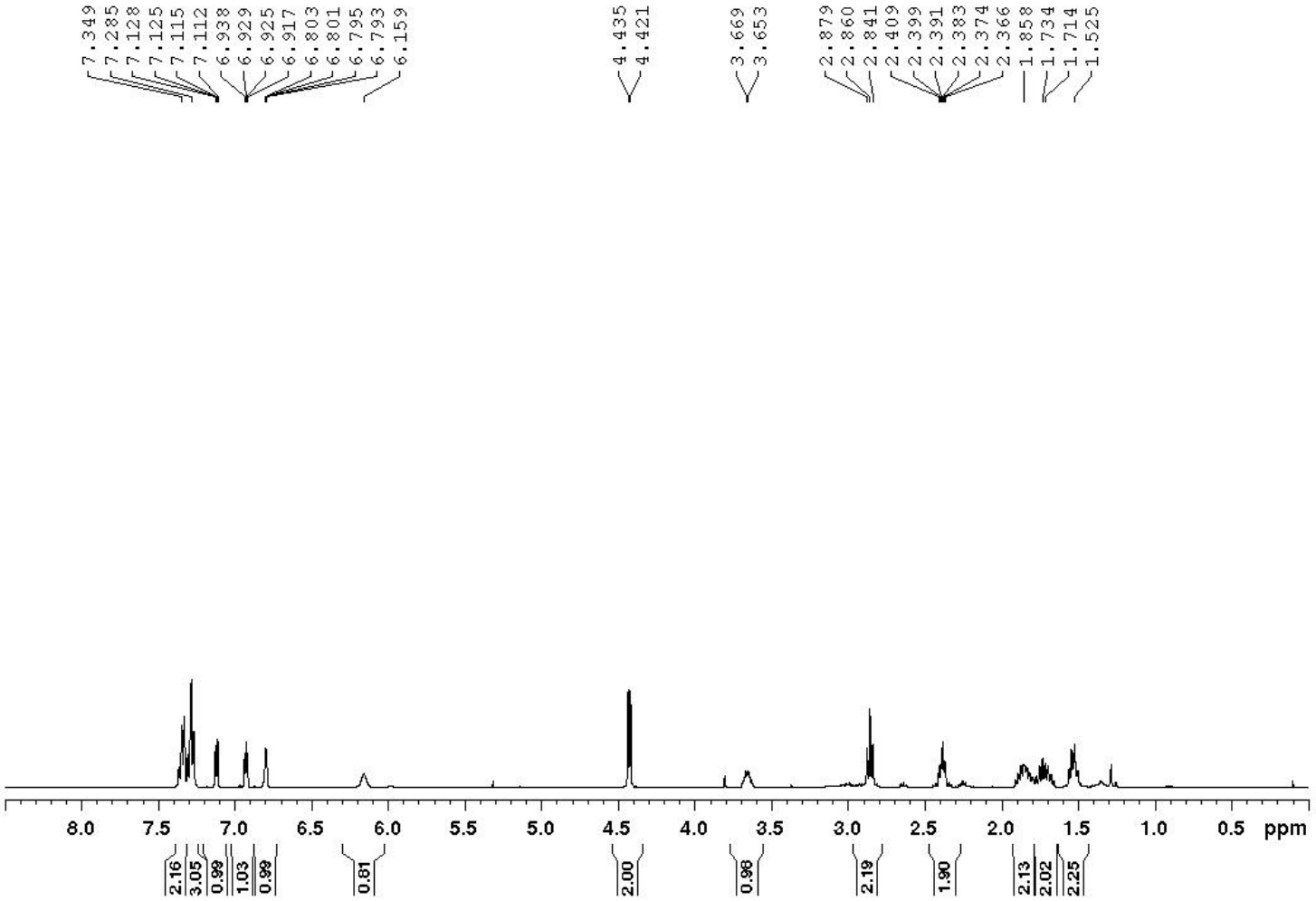


7f

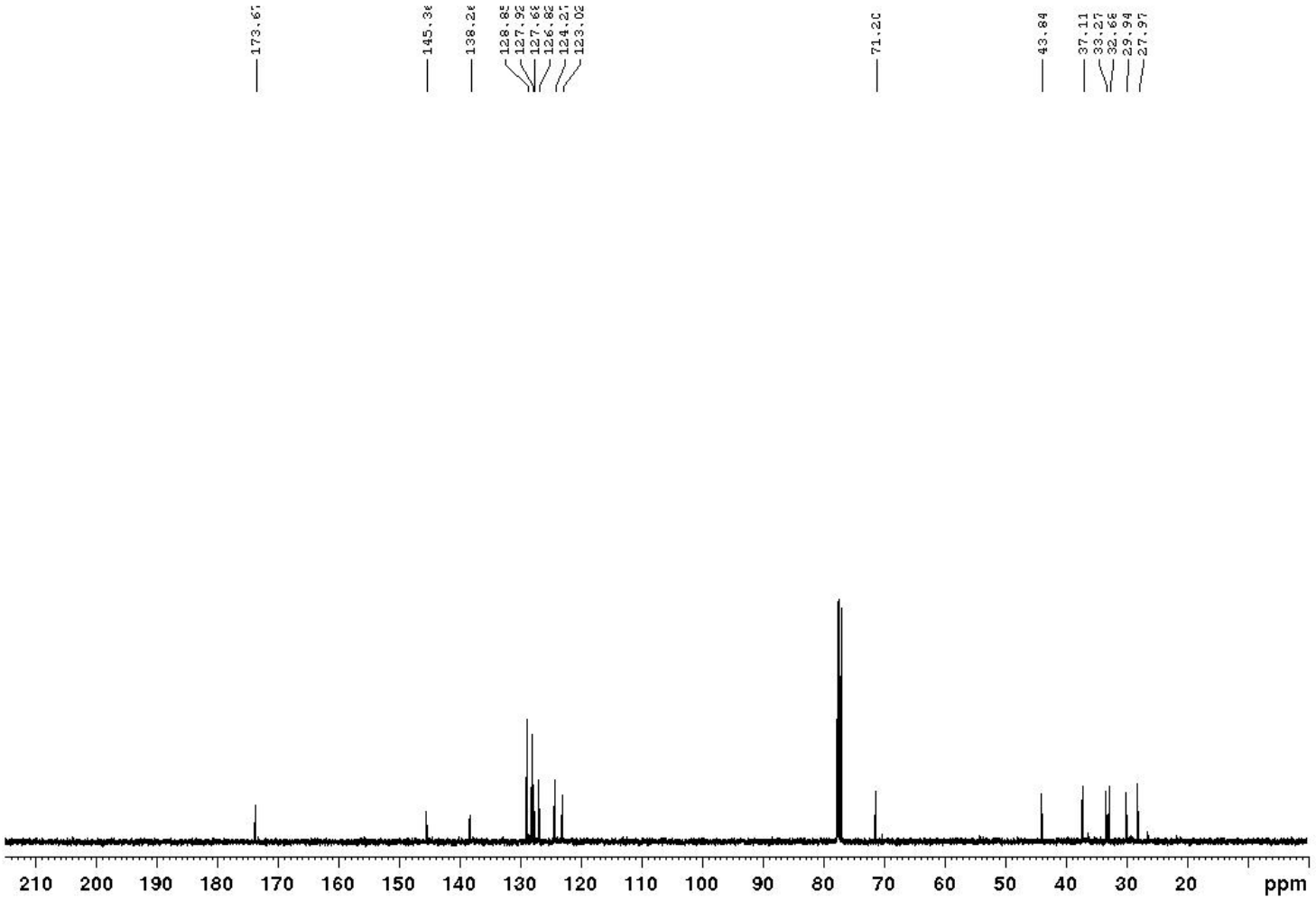


$[\alpha]_D^{20}$	–4.7º (*c* 2.0, $CHCl_3$)
m.p.	73.5–74.5 ºC
TLC analysis	R_f 0.35 (0:100 hexanes:ethyl acetate)
HPLC analysis	Chiral HPLC analysis (Chiralpak-IB, 60:40 hexanes:isopropanol, flowrate = 1.4 mL/min) showed peaks at 28 minutes (94.0% (*S*)) and 109 minutes (6.0% (*R*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.35–7.40 (2H, b,b'), 7.25–7.35 (3H, a,c,c'), 7.12 (1H, dd, *J* = 5.1 and 1.0 Hz, p), 6.93 (1H, dd, *J* = 5.0 and 3.4 Hz, o), 6.80 (1H, dd, *J* = 3.3 and 0.8 Hz, n), 6.16 (1H, br s, NH), 4.43 (2H, d, *J* = 5.7 Hz, e), 3.60–3.70 (1H, m, i), 2.86 (2H, t, *J* = 7.5 Hz, l), 2.39 (2H, td, *J* = 7.2 and 3.8 Hz, g), 1.80–1.90 (2H, m, h,k), 1.65–1.80 (2H, m, h,k), 1.45–1.60 (2H, m, j)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.67 (f), 145.36 (m), 138.26 (d), 128.85 (b,b'), 127.92 (c,c'), 127.68 (a), 126.82 (o), 124.27 (n), 123.02 (p), 71.20 (i), 43.84 (e), 37.11 (j), 33.27 (g), 32.68 (h), 29.94 (l), 27.97 (k)
IR (neat)	3291 (N-H stretch, O-H stretch), 2917, 2849, 1630 (C=O stretch), 1534, 1453, 691 cm^{-1}
HRMS (ESI)	$C_{18}H_{23}NNaO_2S$ (M+Na): 340.1347, found 340.1354 *m/z*

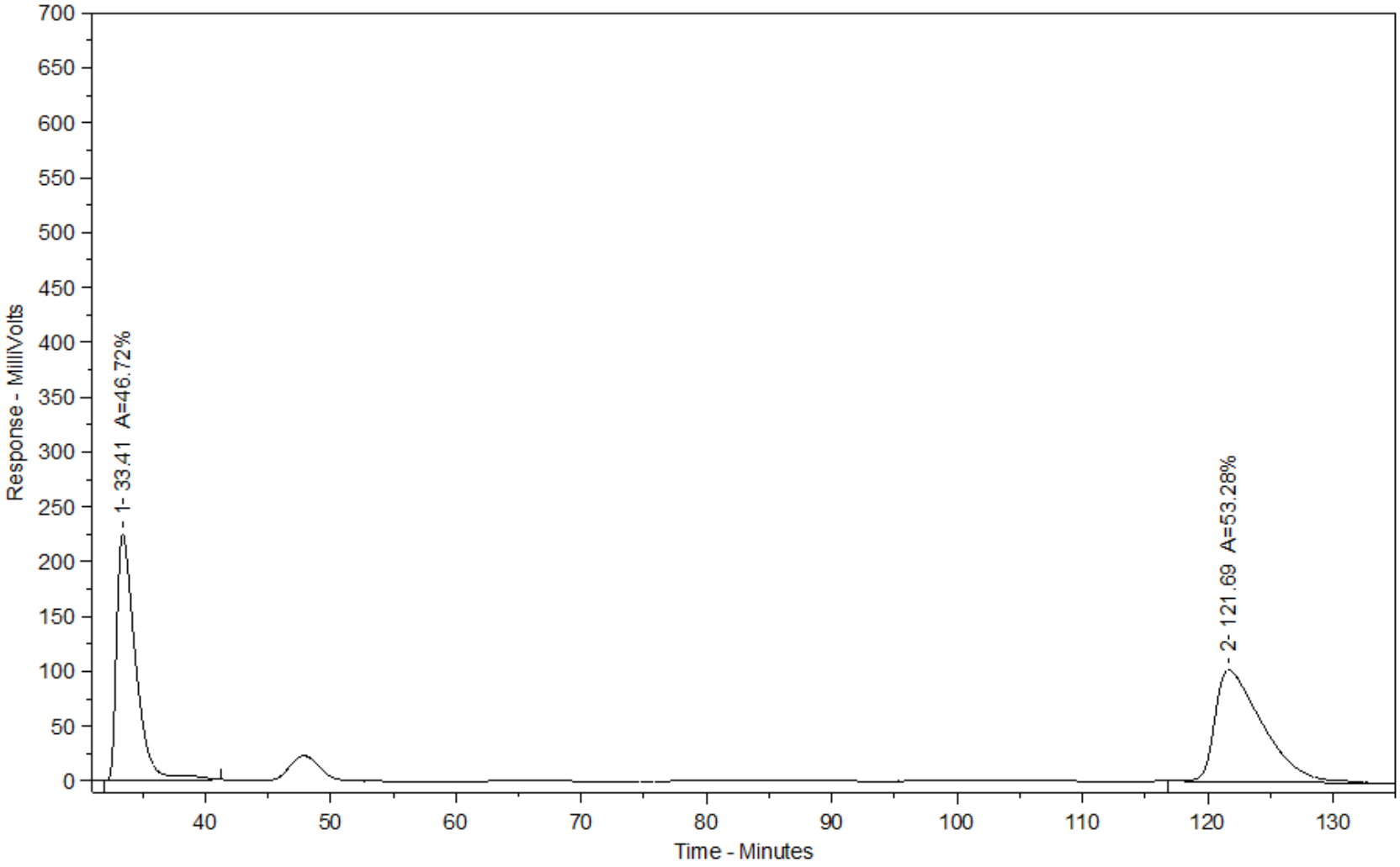
^{1}H NMR of 7f


7.349
7.285
7.128
7.125
7.115
7.112
6.938
6.929
6.925
6.917
6.803
6.801
6.795
6.793
6.159
4.435
4.421
3.669
3.653
2.879
2.860
2.841
2.409
2.399
2.391
2.383
2.374
2.366
1.858
1.734
1.714
1.525
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.16
3.05
0.99
1.03
0.99
0.81
2.00
0.96
2.19
1.90
2.13
2.02
2.25

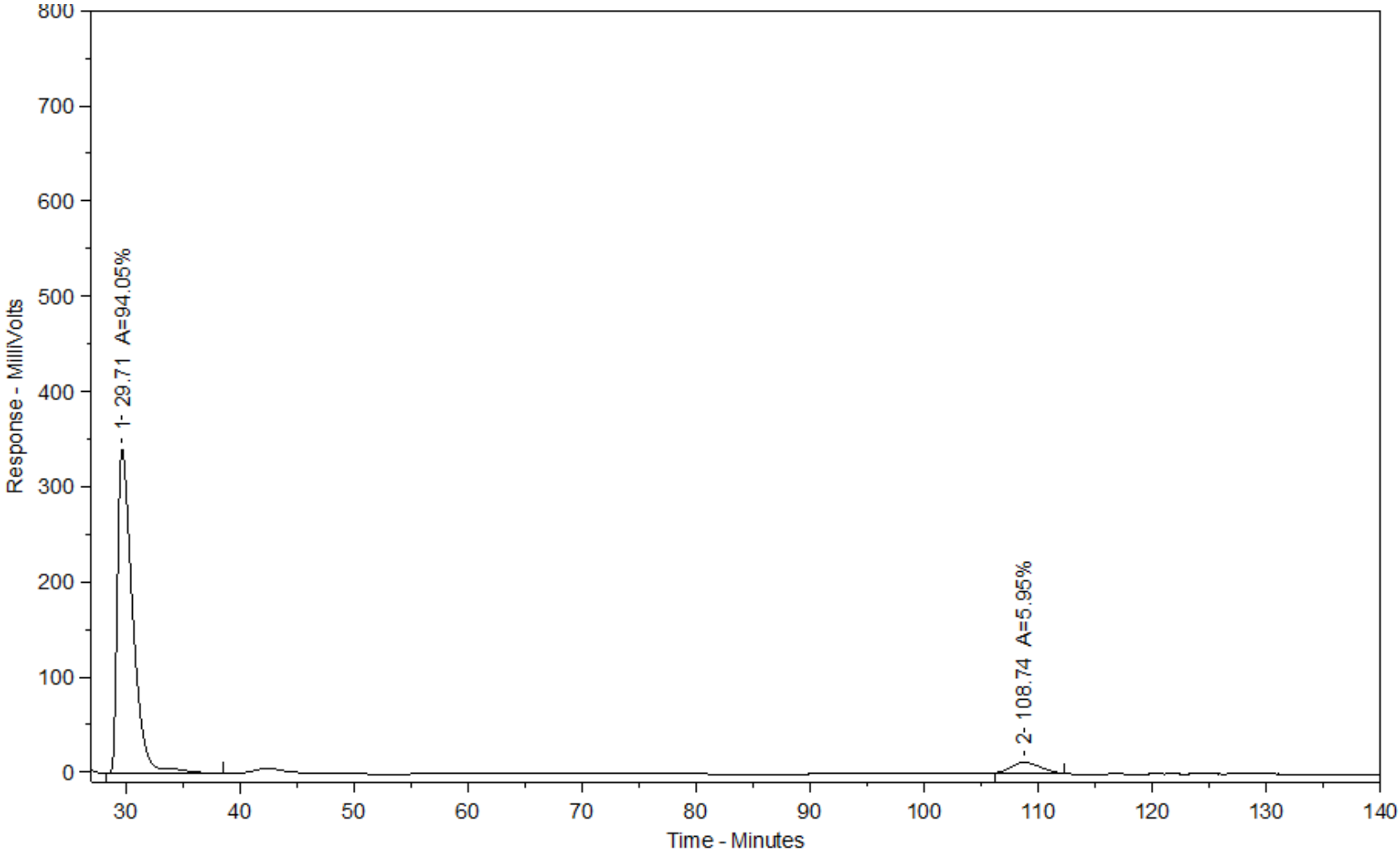
^{13}C NMR of 7f


173.67
145.36
138.24
128.85
127.92
127.68
126.82
124.27
123.02
71.20
43.84
37.11
33.27
32.68
29.94
27.97
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

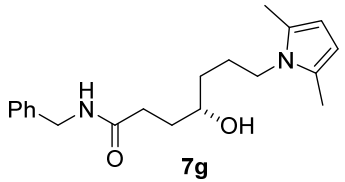
HPLC trace of 7f

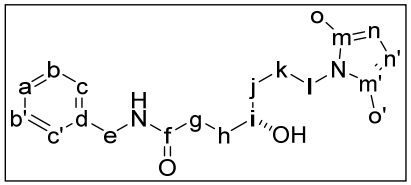


Racemic **7f**


Response - MilliVolts
Time - Minutes
1- 29.71 A=94.05%
2- 108.74 A=5.95%
800
700
600
500
400
300
200
100
0
30
40
50
60
70
80
90
100
110
120
130
140

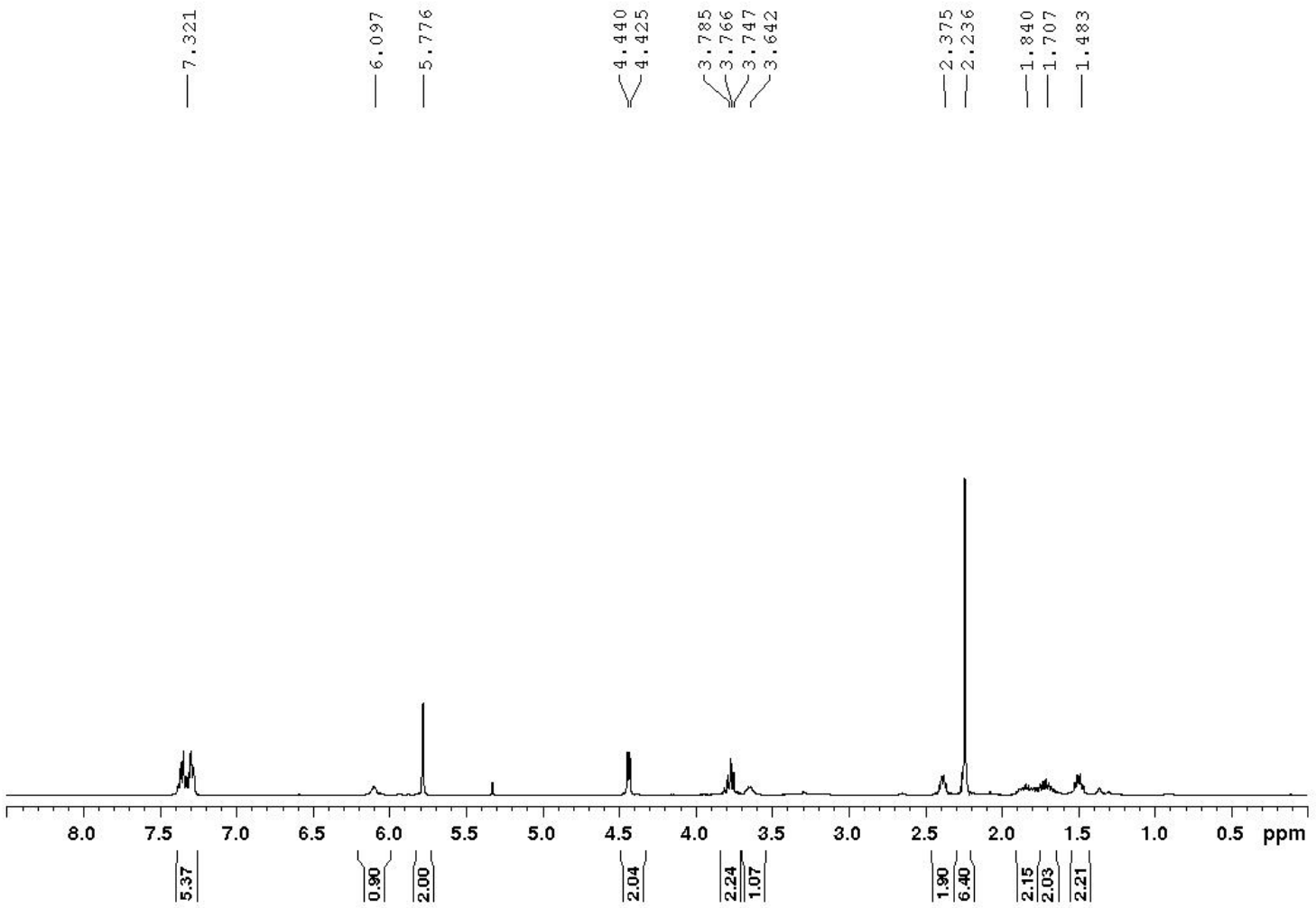
(*S*)-**7f**



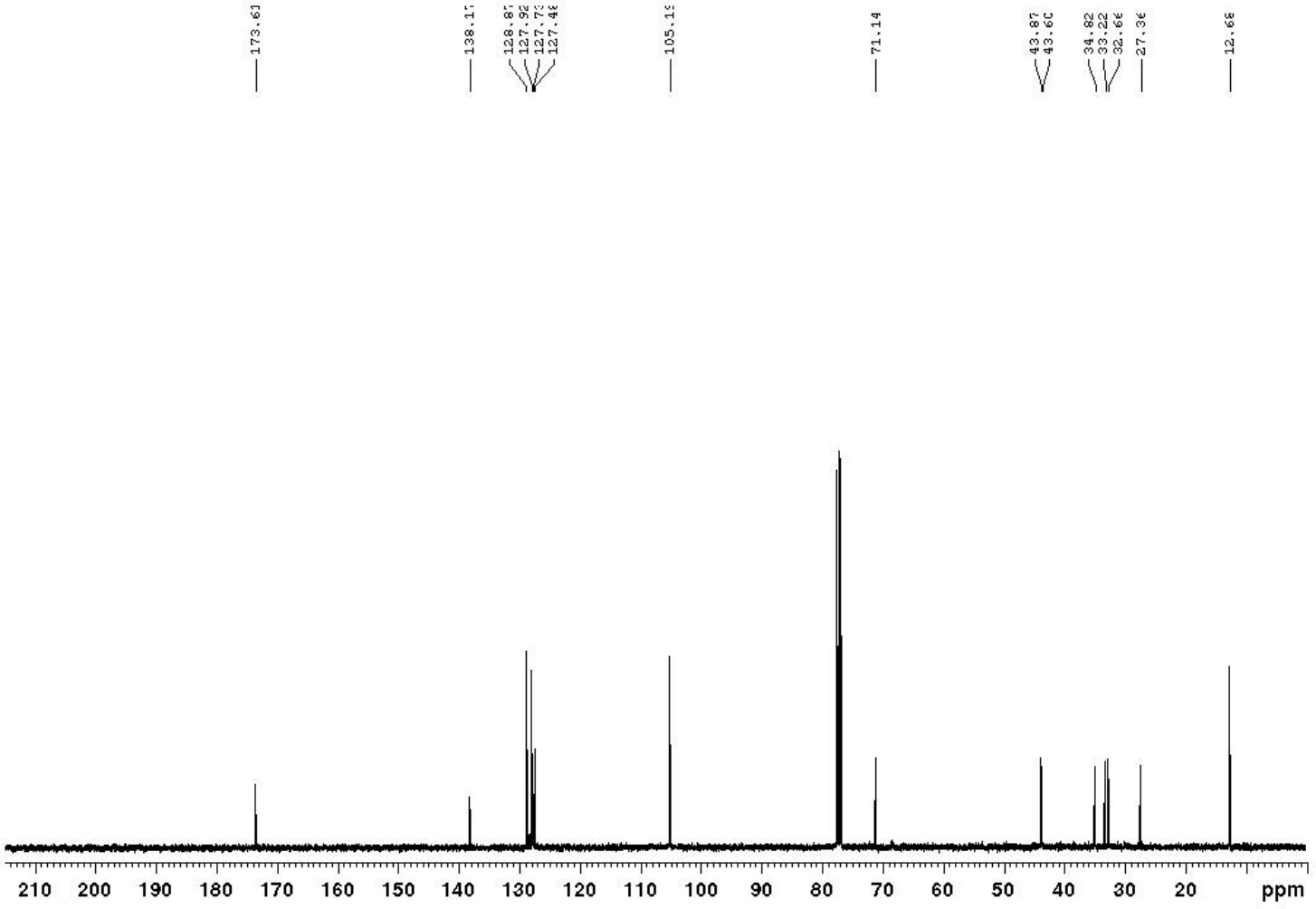


$[\alpha]_D^{20}$	–7.1° (*c* 1.8, $CHCl_3$)
TLC analysis	R_f 0.4 (0:100 hexanes:ethyl acetate)
HPLC analysis	Chiral HPLC analysis (Chiralpak-IC, 60:40 hexanes:isopropanol, flowrate = 1.4 mL/min) showed peaks at 42 minutes (8.0% (*R*)) and 54 minutes (92.0% (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.40 (5H, a,b,b',c,c'), 6.10 (1H, br s, NH), 5.78 (2H, s, n,n'), 4.43 (2H, d, *J* = 5.7 Hz, e), 3.77 (2H, t, *J* = 7.6 Hz, l), 3.55–3.70 (1H, m, i), 2.30–2.45 (2H, m, g), 2.24 (6H, s, o,o'), 1.75–1.90 (2H, m, h,k), 1.65–1.75 (2H, m, h,k), 1.45–1.55 (2H, m, j)
^{13}C NMR (100 MHz, $CDCl_3$)	173.61 (f), 138.17 (d), 128.87 (b,b'), 127.92 (c,c'), 127.72 (a), 127.48 (m,m'), 105.19 (n,n'), 71.14 (i), 43.87 (e), 43.60 (l), 34.82 (j), 33.22 (g), 32.66 (h), 27.36 (k), 12.68 (o,o')
IR (neat)	3285 (N-H stretch, O-H stretch), 2923, 1643 (C=O stretch), 1541, 1453, 1407, 1298, 742, 697 cm^{-1}
HRMS (ESI)	$C_{20}H_{28}N_2NaO_2$ (M+Na): 351.2048, found 351.2059 *m/z*

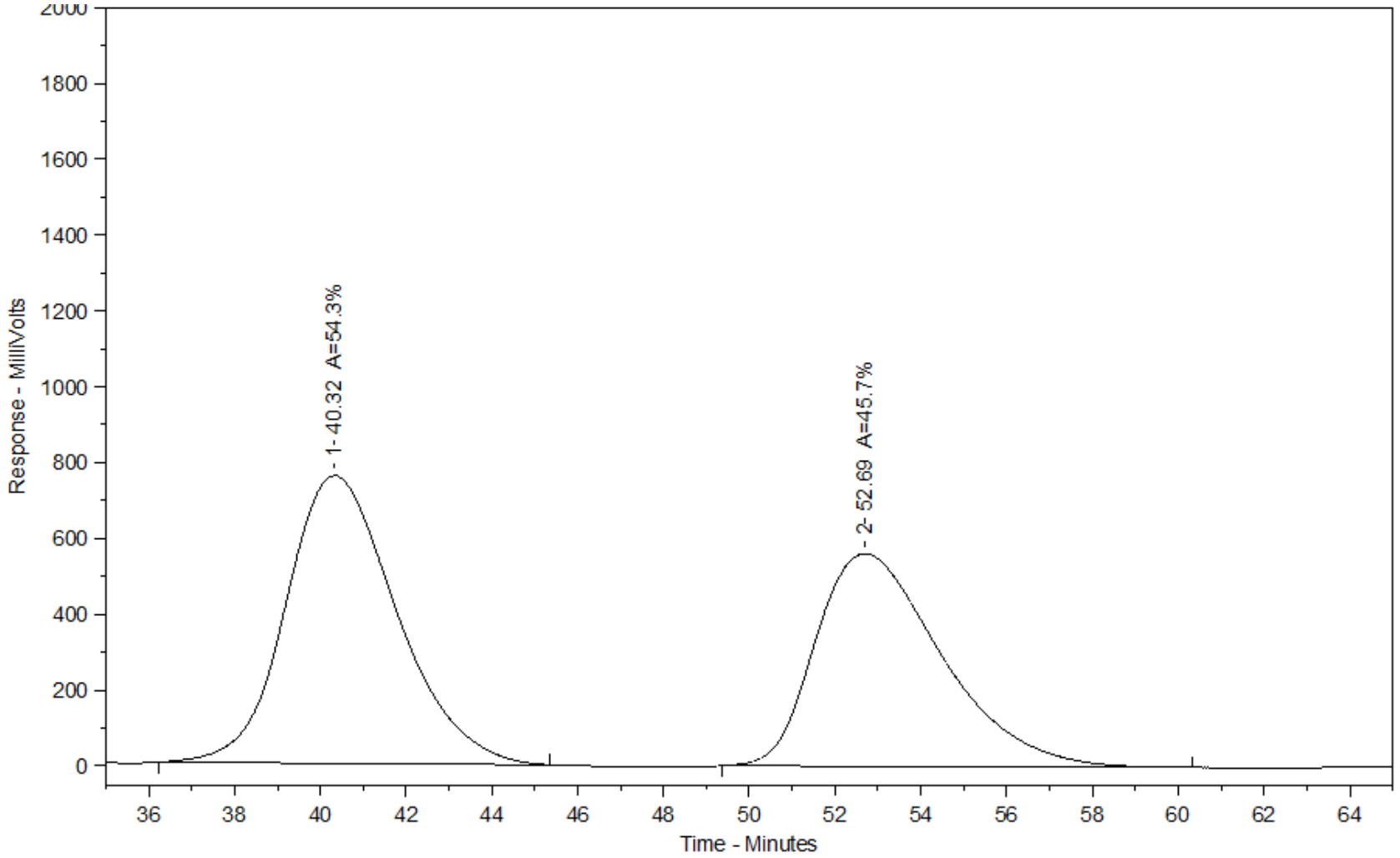
^{1}H NMR of 7g


7.321
6.097
5.776
4.440
4.425
3.785
3.766
3.747
3.642
2.375
2.236
1.840
1.707
1.483
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.37
0.90
2.00
2.04
2.24
1.07
1.90
6.40
2.15
2.03
2.21

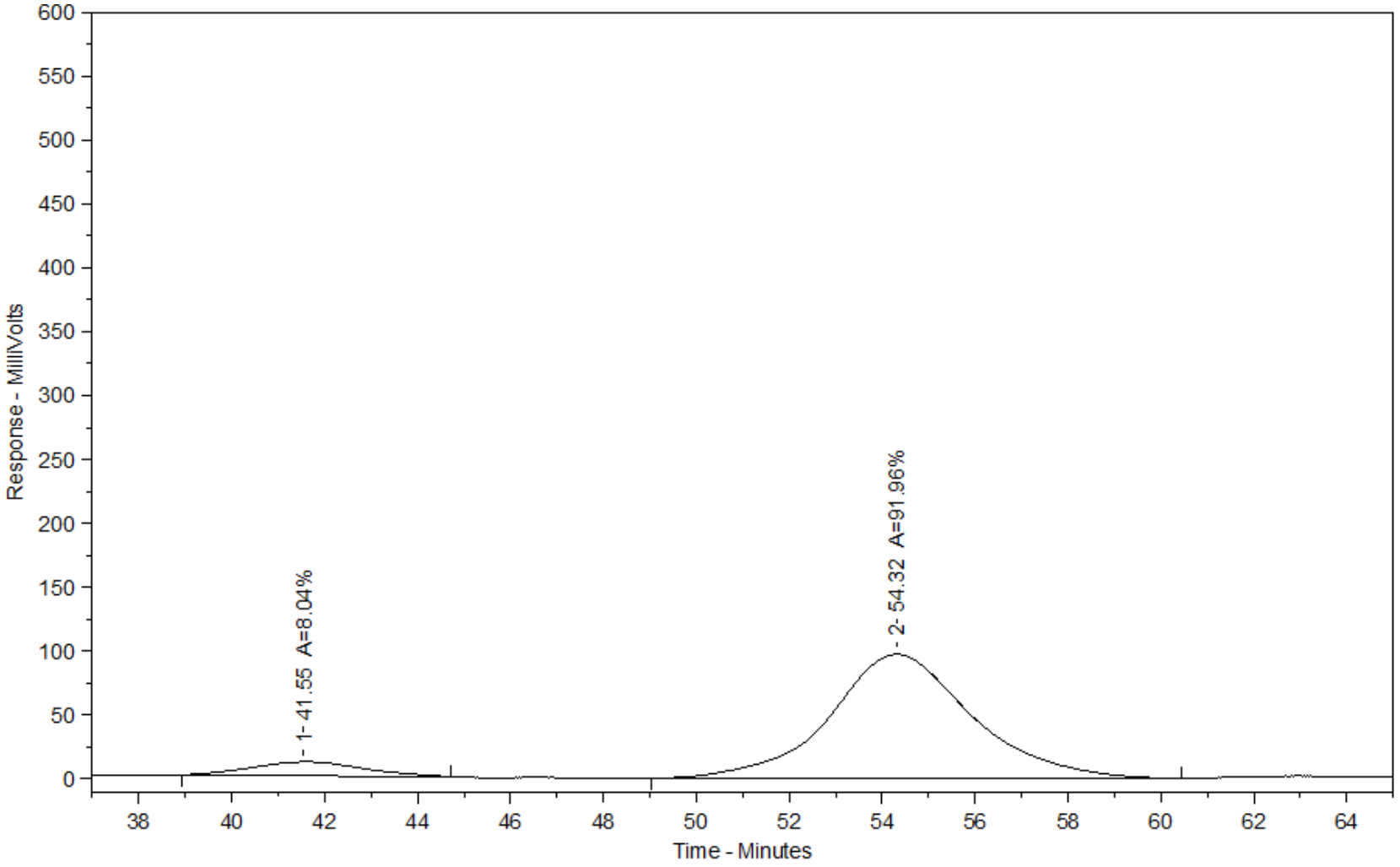
^{13}C NMR of 7g


173.61
138.17
128.87
127.98
127.73
127.48
105.19
71.14
43.87
43.60
34.82
33.22
32.66
27.36
12.66
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

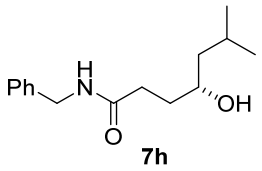
HPLC trace of 7g



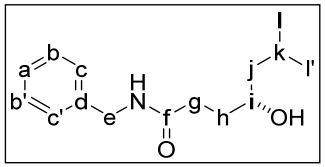
Racemic **7g**



(*S*)-**7g**

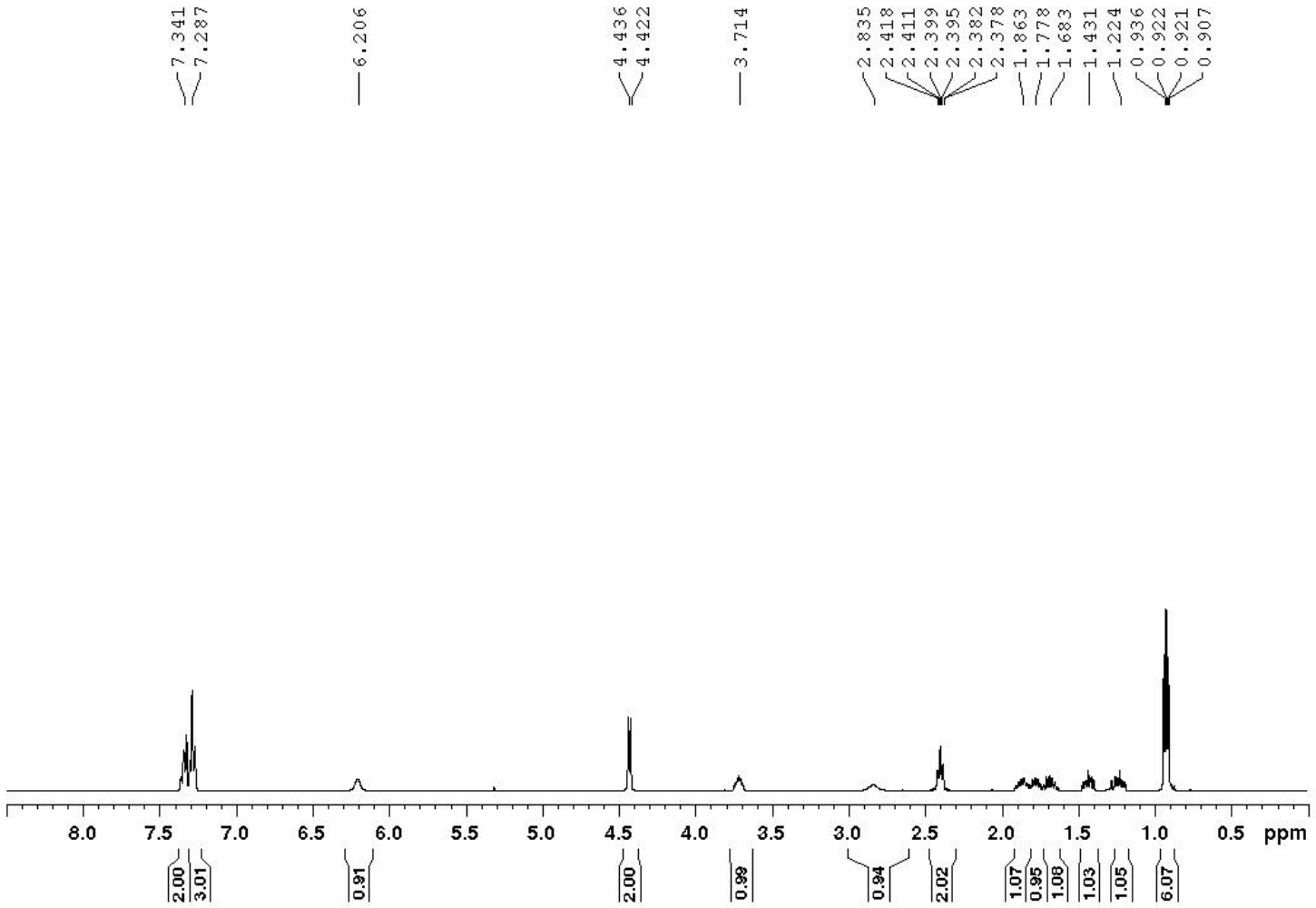


7h

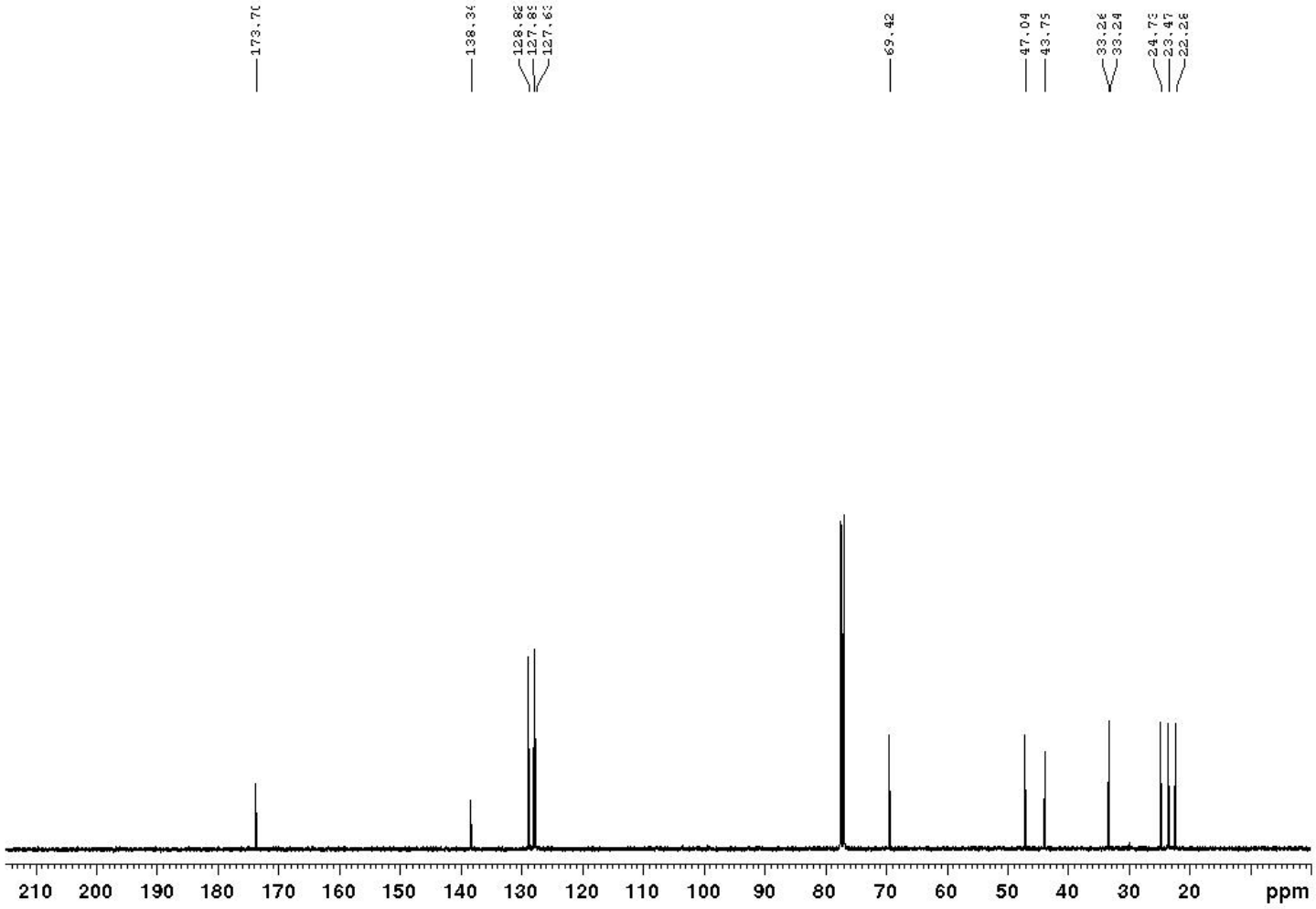


$[\alpha]_D^{20}$	–18.4º (*c* 2.0, $CHCl_3$)
m.p.	50.5–51.5 ºC
TLC analysis	R_f 0.4 (0:100 hexanes:ethyl acetate)
HPLC analysis	Chiral HPLC analysis (Chiralpak-IC, 90:10 hexanes:isopropanol, flowrate = 1.4 mL/min) showed peaks at 96 minutes (3.0% (*R*)) and 103 minutes (97.0% (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.40 (2H, b,b'), 7.25–7.30 (3H, a,c,c'), 6.21 (1H, br s, NH), 4.43 (2H, d, *J* = 5.7 Hz, e), 3.65–3.75 (1H, m, i), 2.60–3.00 (1H, br s, OH), 2.40 (2H, td, *J* = 7.6 and 2.6 Hz, g), 1.80–1.90 (1H, m, h), 1.70–1.80 (1H, m, k), 1.60–1.70 (1H, m, h), 1.40–1.50 (1H, m, j), 1.20–1.25 (1H, m, j), 0.92 (6H, dd, *J* = 6.2 and 5.4 Hz, l,l')
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.70 (f), 138.34 (d), 128.82 (b,b'), 127.89 (c,c'), 127.63 (a), 69.42 (i), 47.04 (j), 43.79 (e), 33.26 (h), 33.24 (g), 24.73 (k), 23.47 and 22.28 (l.l')
IR (neat)	3284 (N-H stretch, O-H stretch), 2952, 2916, 2868, 1643 (C=O stretch), 1546, 1453, 696 cm^{-1}
HRMS (ESI)	$C_{15}H_{23}NNaO_2$ (M+Na): 272.1626, found 272.1638 *m/z*

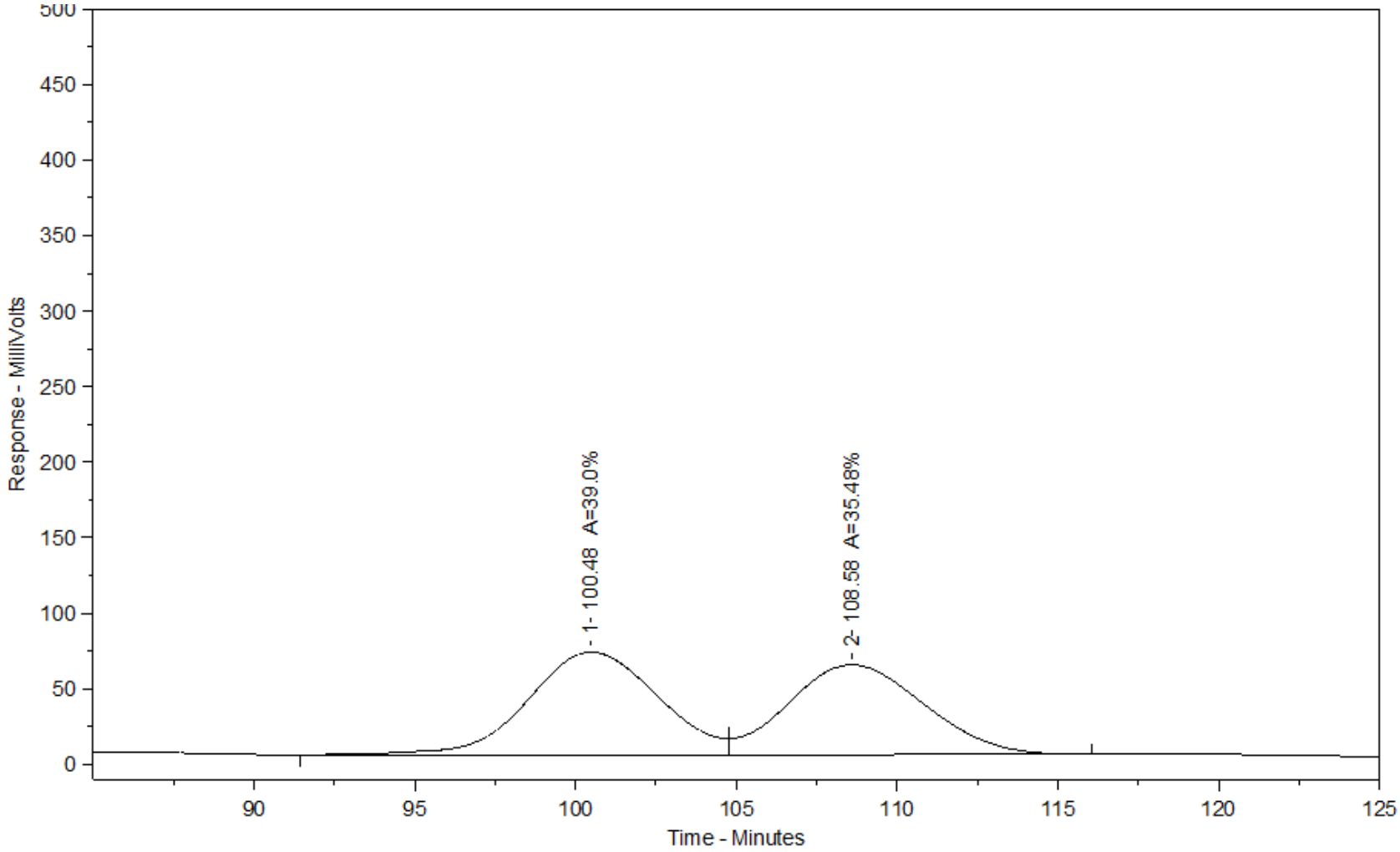
^{1}H NMR of 7h


7.341
7.287
6.206
4.436
4.422
3.714
2.835
2.418
2.411
2.399
2.395
2.382
2.378
1.863
1.778
1.683
1.431
1.224
0.936
0.922
0.921
0.907
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
3.01
0.91
2.00
0.99
0.94
2.02
1.07
0.95
1.08
1.03
1.05
6.07

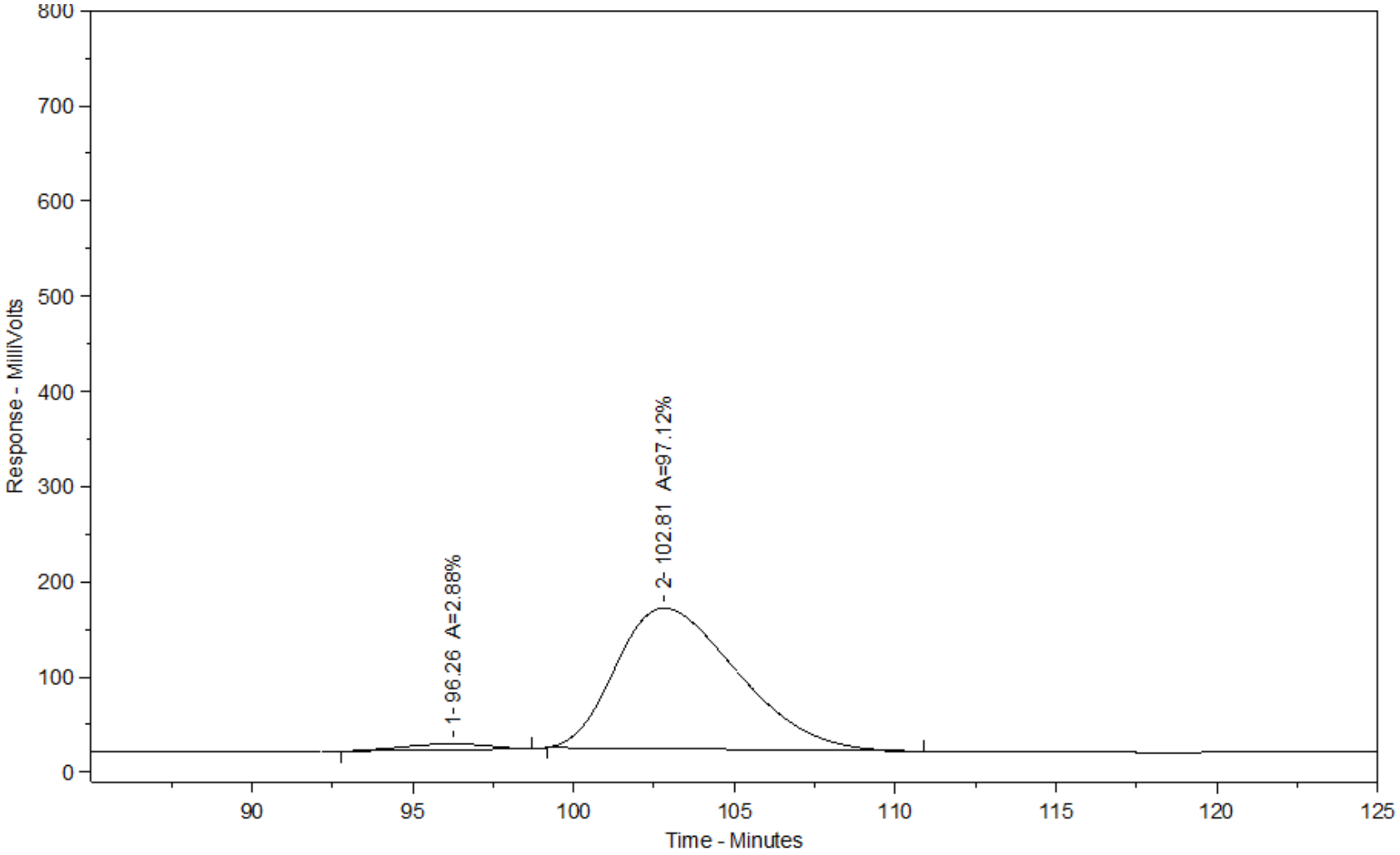
^{13}C NMR of 7h


69.42
47.04
43.75
33.26
33.24
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

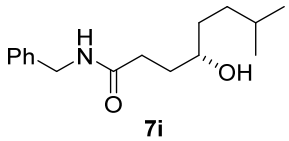
HPLC trace of 7h



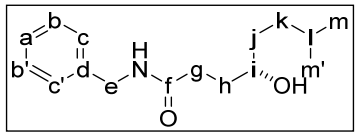
Racemic **7h**


Response - MilliVolts
Time - Minutes
1 - 96.26 A=2.88%
2 - 102.81 A=97.12%
0
100
200
300
400
500
600
700
800
90
95
100
105
110
115
120
125

(*S*)-**7h**

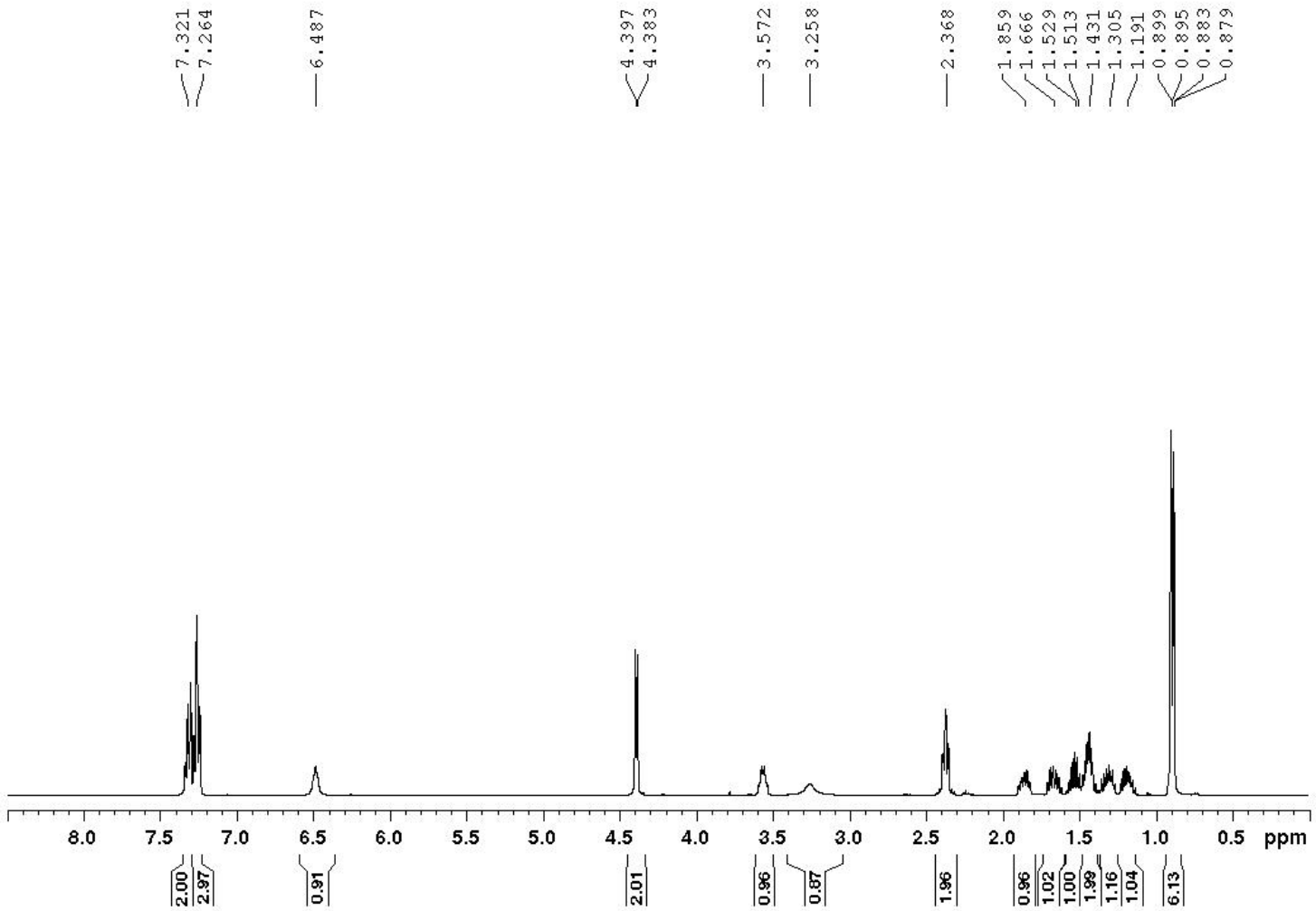


7i

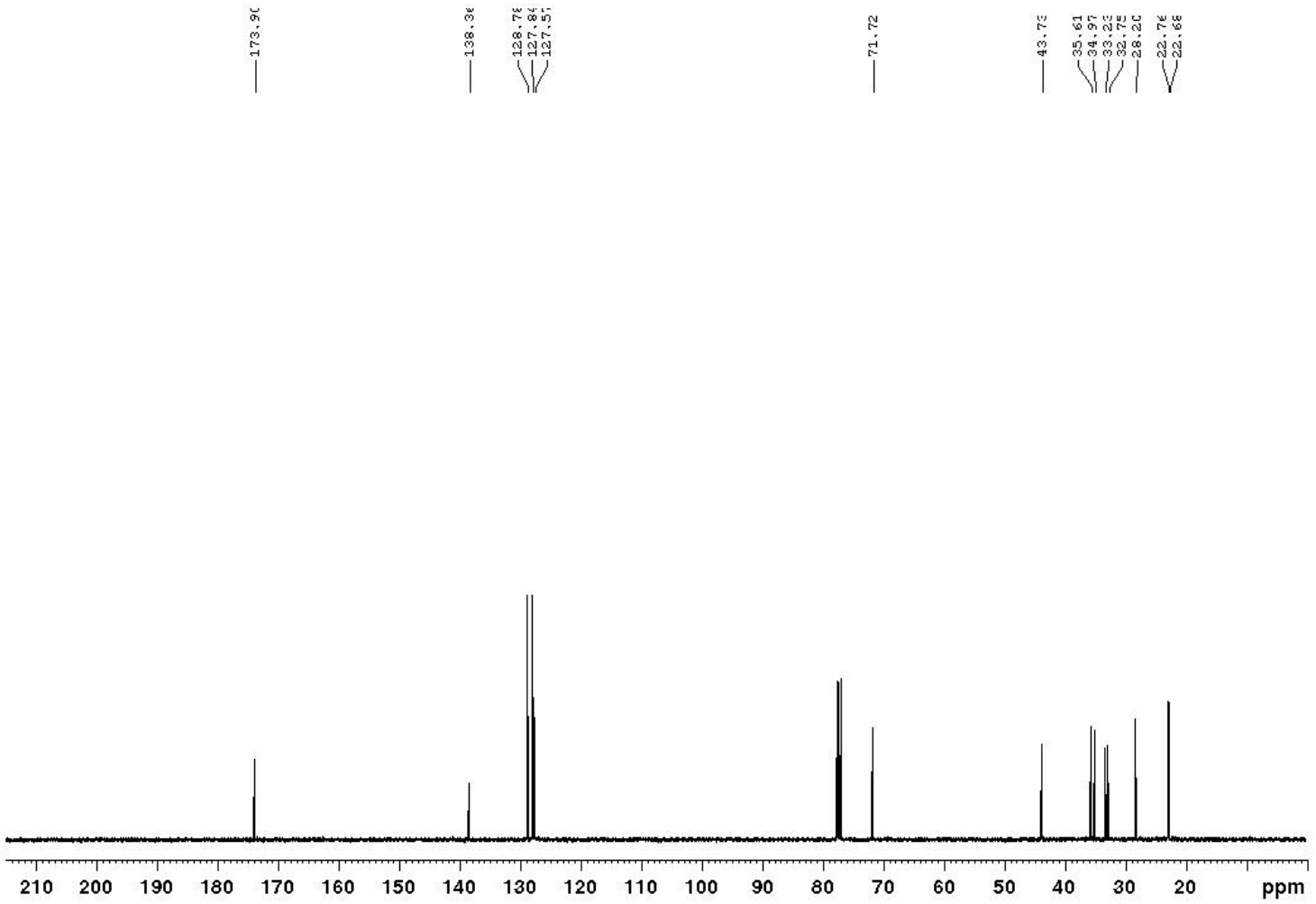


$[\alpha]_D^{20}$	–5.9º (*c* 2.0, $CHCl_3$)
m.p.	61.0–62.0 ºC
TLC analysis	R_f 0.4 (0:100 hexanes:ethyl acetate)
HPLC analysis	Chiral HPLC analysis (Chiralcel-OD, 60:40 hexanes:isopropanol, flowrate = 1.0 mL/min) showed peaks at 11 minutes (96.5% (*S*)) and 16 minutes (3.5% (*R*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.35 (2H, b,b'), 7.20–7.30 (a,c,c'), 6.49 (1H, br s, NH), 4.39 (2H, d, *J* = 5.7 Hz, e), 3.50–3.60 (1H, m, i), 3.26 (1H, br s, OH), 2.30–2.45 (2H, m, g), 1.80–1.90 (1H, m, h), 1.60–1.70 (1H, m, h), 1.50–1.60 (1H, m, l), 1.40–1.50 (2H, m, j), 1.25–1.35 (1H, m, k), 1.15–1.25 (1H, m, k) 0.89 (6H, dd, *J* = 6.6 and 1.6 Hz, m,m')
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.90 (f), 138.36 (d), 128.78 (b,b'), 127.84 (c,c'), 127.57 (a), 71.72 (i), 43.72 (e), 35.60 (j), 34.97 (k), 33.23 (g), 32.75 (h), 28.20 (l), 22.76 and 22.68 (m,m')
IR (neat)	3452 (N-H stretch), 3294 (O-H stretch), 2951. 2931, 2901, 2868, 1615 (C=O stretch), 1545, 1454, 1249, 1063, 1029, 723, 692 cm^{-1}
HRMS (ESI)	$C_{16}H_{25}NNaO_2$ (M+Na): 286.1783, found 286.1785 *m/z*

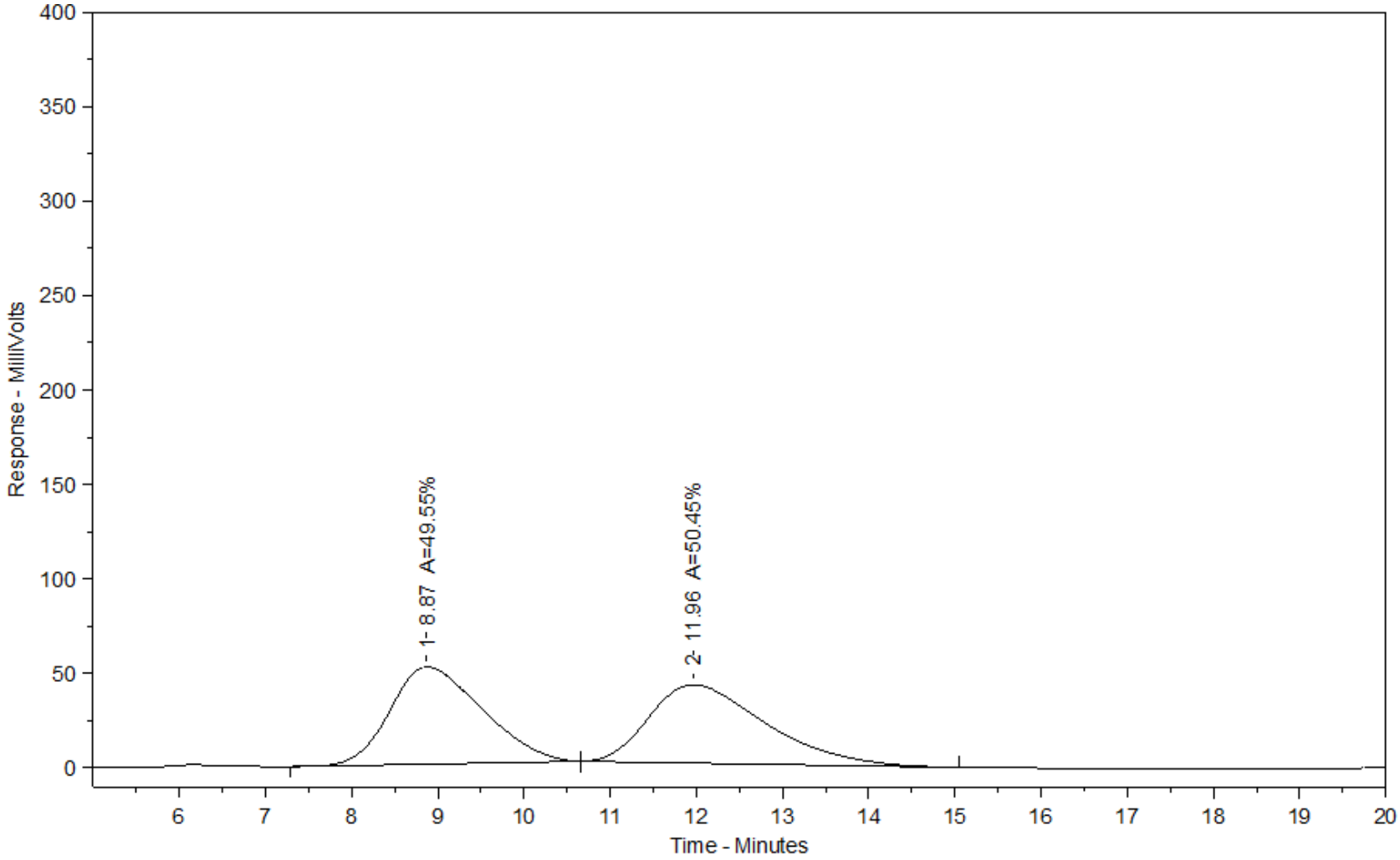
^{1}H NMR of 7i


7.321
7.264
6.487
4.397
4.383
3.572
3.258
2.368
1.859
1.666
1.529
1.513
1.431
1.305
1.191
0.899
0.895
0.883
0.879
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.00
2.97
0.91
2.01
0.96
0.87
1.96
0.96
1.02
1.00
1.99
1.16
1.04
6.13

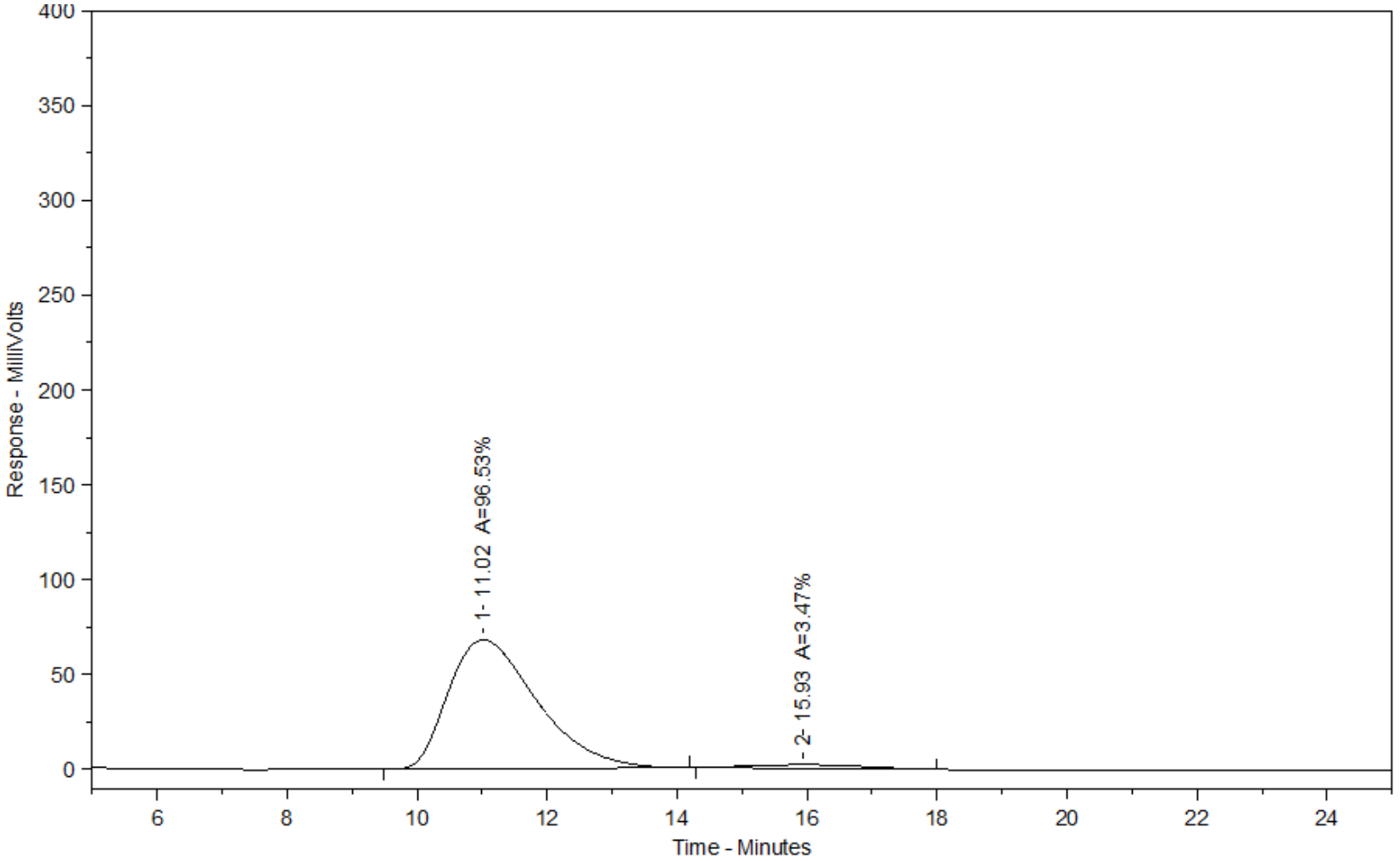
^{13}C NMR of 7i


173.90
138.38
128.78
127.84
127.51
71.72
43.73
35.61
34.97
33.23
32.75
28.20
22.78
22.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

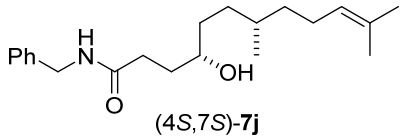
HPLC trace of 7i



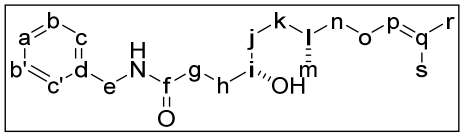
Racemic of **7i**


Response - MilliVolts
Time - Minutes
1- 11.02 A=96.53%
2- 15.93 A=3.47%
400
350
300
250
200
150
100
50
0
6
8
10
12
14
16
18
20
22
24

(*S*)-**7i**

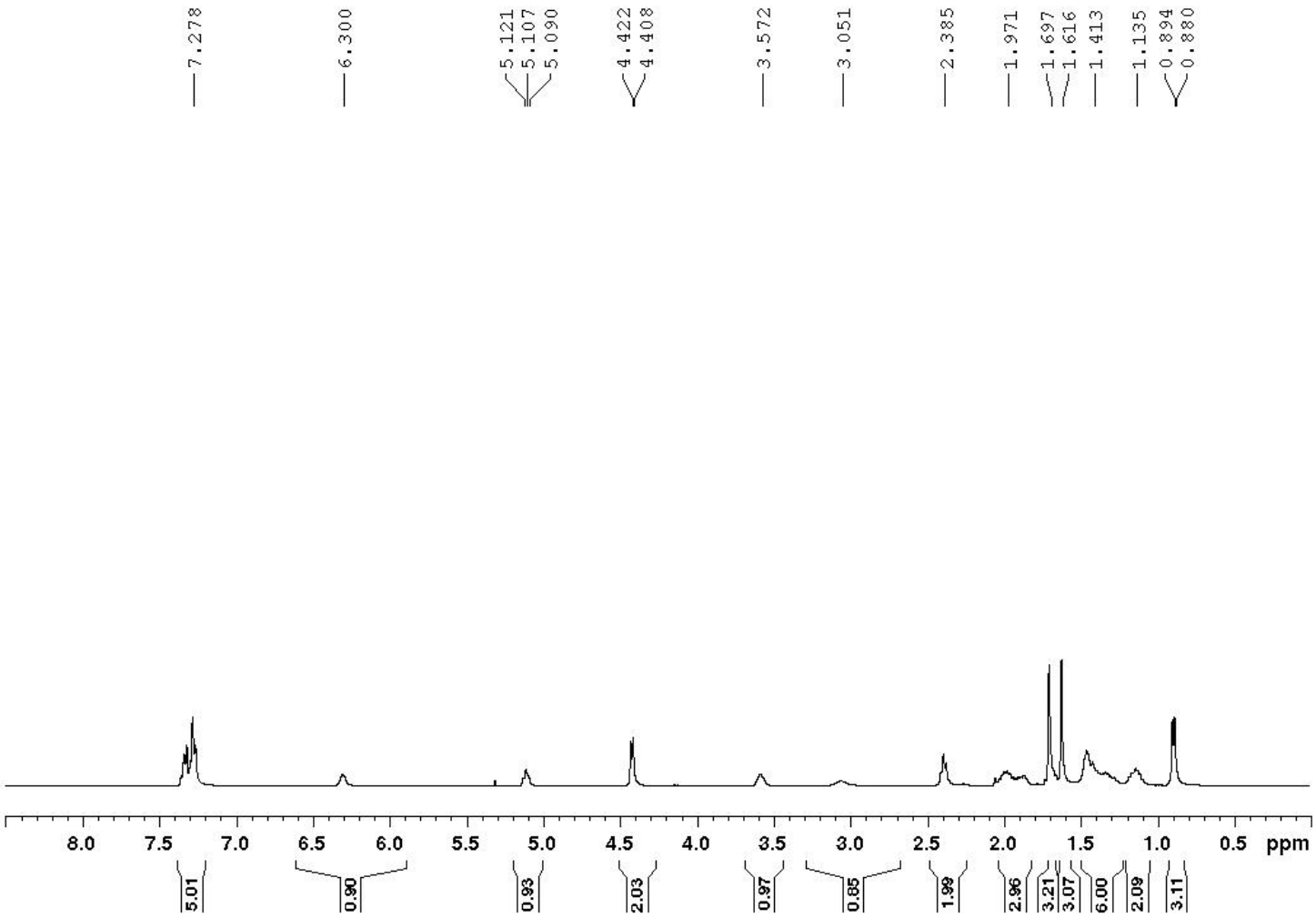


(4*S*,7*S*)-**7j**

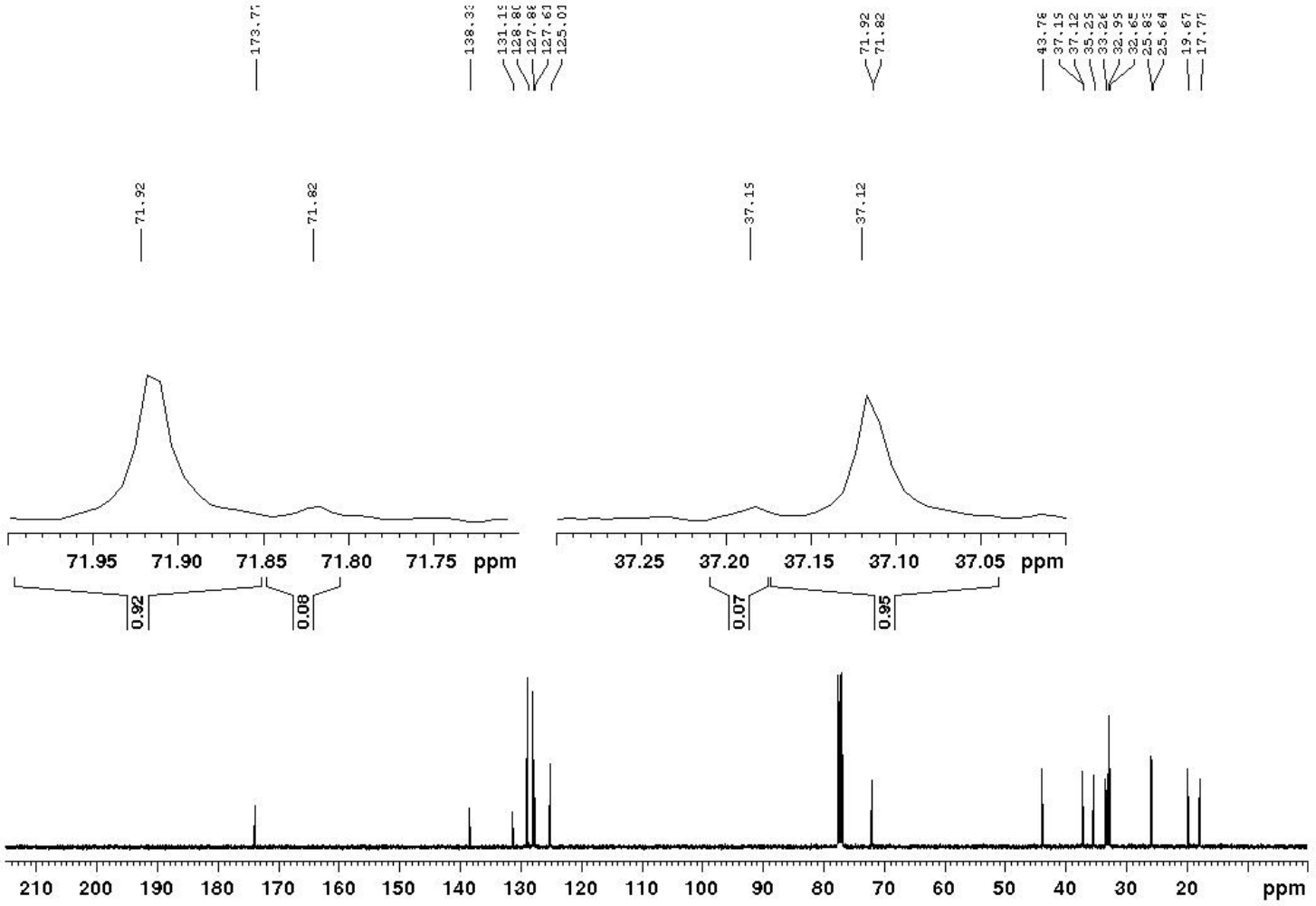


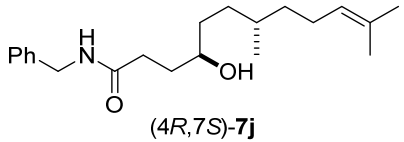
$[\alpha]_D^{20}$	–2.5° (*c* 1.0, $CHCl_3$)
m.p.	72.0–73.0 ºC
TLC analysis	R_f 0.5 (0:100 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.20–7.40 (5H, a,b,b',c,c'), 6.30 (1H, br s, NH), 5.11 (1H, t, *J* = 5.8 Hz, p), 4.42 (2H, d, *J* = 5.5 Hz, e), 3.45–3.65 (1H, m, i), 3.05 (1H. br s, OH), 2.30–2.45 (2H, m, g), 1.80–2.05 (3H, m, o,h), 1.70 (3H, s, r), 1.62 (3H, s, s), 1.20–1.50 (6H, m, h,j,l,n), 1.15–1.20 (2H, m, k), 0.89 (3H, d, *J* = 5.5 Hz, m)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.77 (f), 138.33 (d), 131.19 (q), 128.80 (b,b'), 127.88 (c,c'), 127.61 (a), 125.01 (p), 71.92 (major diastereomer, 92%, i), 71.82 (minor diastereomer, 8%, i), 43.78 (e), 37.19 (minor diastereomer, 7%, l), 37.12 (major diastereomer, 93%, l), 35.29 (n), 33.26 (g), 32.99 (h), 32.65 (j and k *overlapping*), 25.83 (r), 25.64 (o), 19.67 (m), 17.77 (s)
IR (neat)	3300 (N-H stretch, O-H stretch), 2962, 2911, 2849, 1642 (C=O stretch), 1552, 1452, 1344, 1256, 695 cm^{-1}
HRMS (ESI)	$C_{21}H_{33}NNaO_2$ (M+Na): 354.2409, found 354.2414 *m/z*

^{1}H NMR of (4*S*,7*S*)-7j

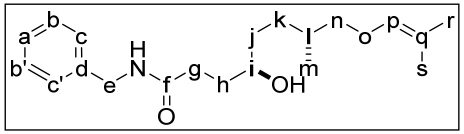


^{13}C NMR of (4*S*,7*S*)-7j



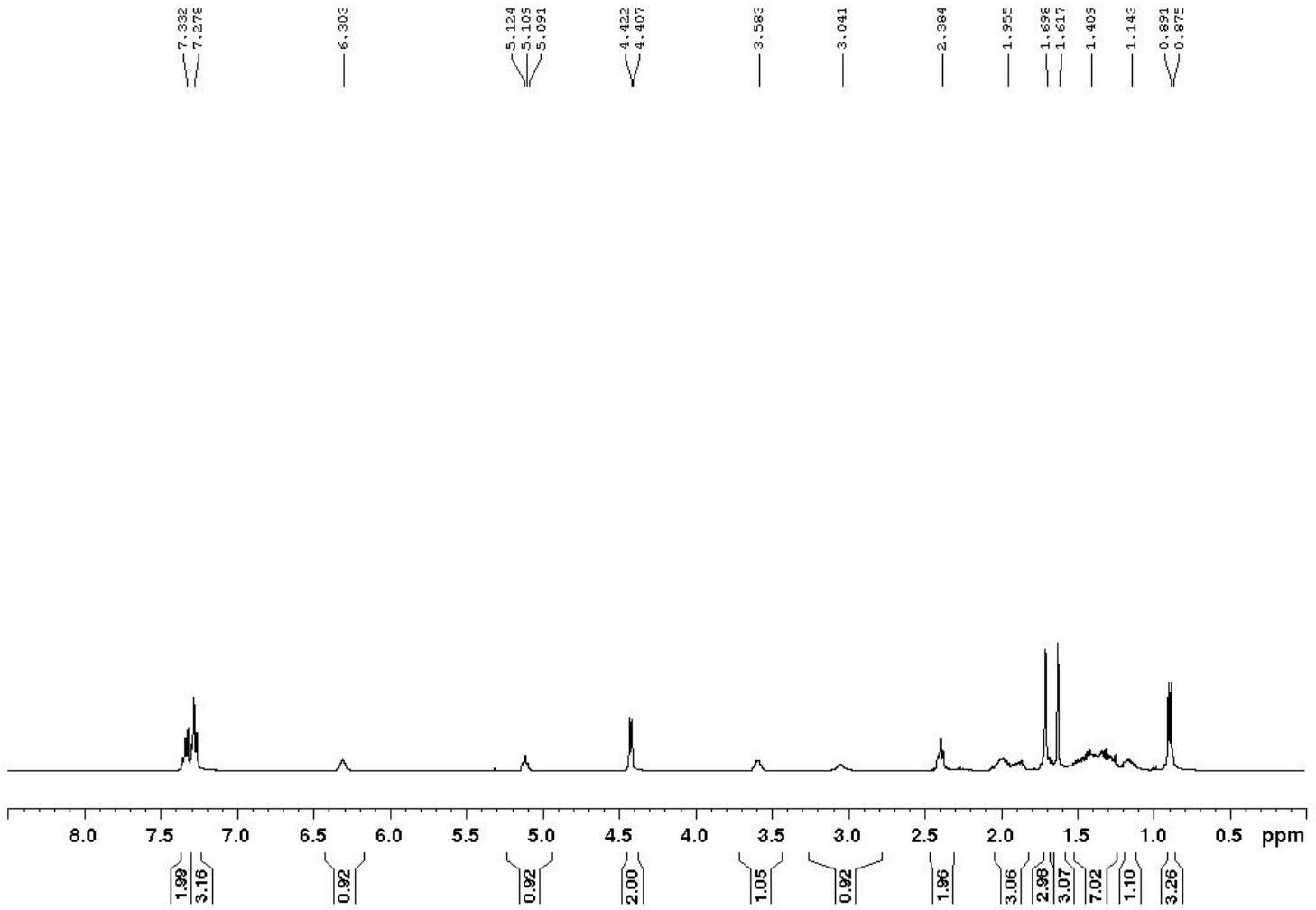


(4*R*,7*S*)-**7j**

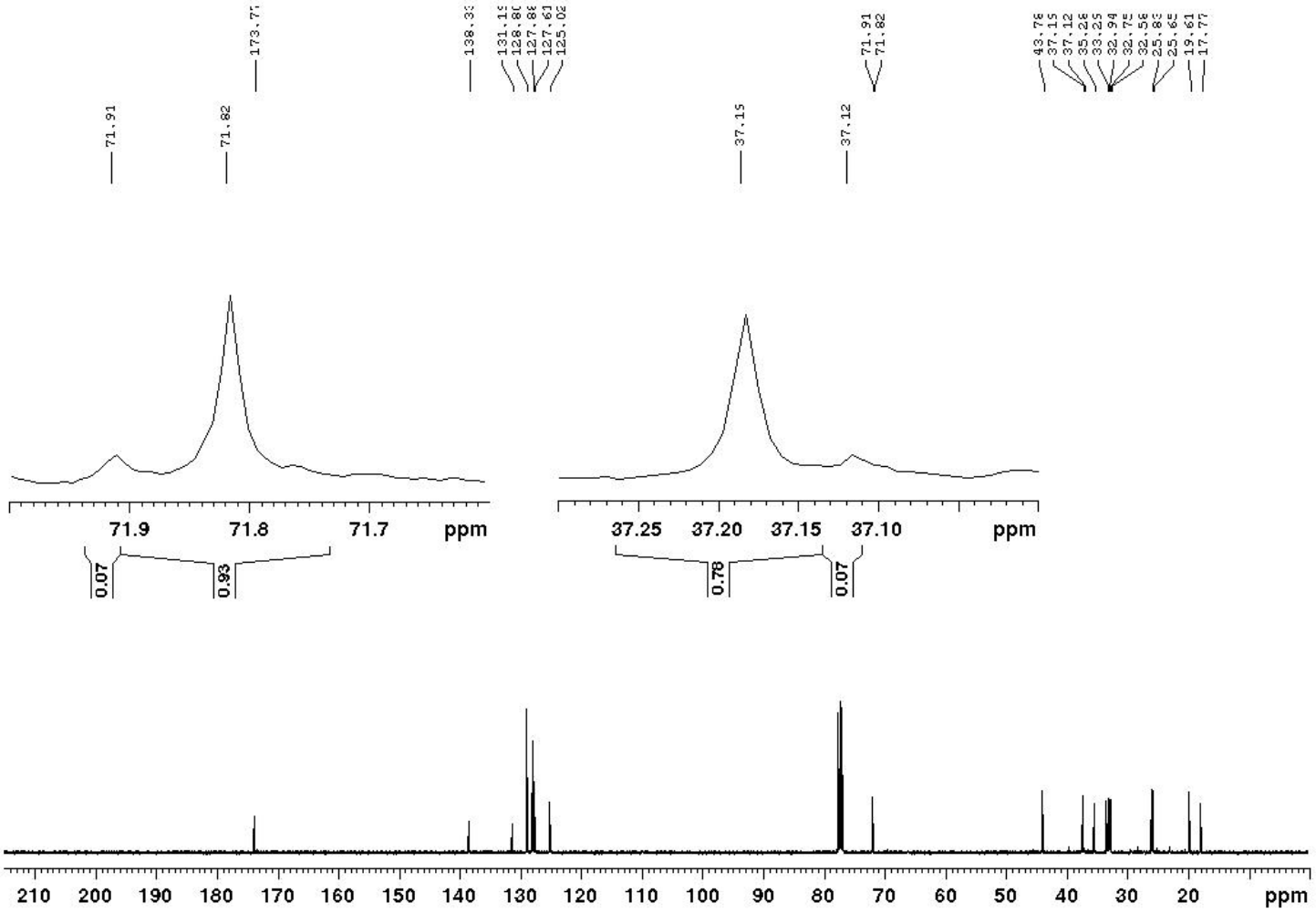


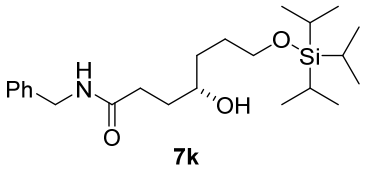
$[\alpha]_D^{20}$	+6.5° (*c* 1.0, $CHCl_3$)
TLC analysis	R_f 0.5 (0:100 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.35 (2H, m, b,b'), 7.25–7.30 (3H, m, a,c,c'), 6.30 (1H, br s, NH), 5.11 (1H, t, *J* = 6.2 Hz, p), 4.42 (2H, d, *J* = 5.7 Hz, e), 3.45–3.70 (1H, m, i), 3.04 (1H. br s, OH), 2.30–2.45 (2H, m, g), 1.80–2.05 (3H, m, o,h), 1.70 (3H, s, r), 1.62 (3H, s, s), 1.20–1.50 (7H, m, h,j,k,l,n), 1.10–1.20 (1H, m, k), 0.89 (3H, d, *J* = 6.4 Hz, m)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.77 (f), 138.33 (d), 131.19 (q), 128.80 (b,b'), 127.88 (c,c'), 127.61 (a), 125.02 (p), 71.92 (minor diastereomer, 7%, i), 71.82 (major diastereomer, 93%, i), 43.78 (e), 37.19 (major diastereomer, 92%, l), 37.12 (minor diastereomer, 8%, l), 35.28 (n), 33.29 (g), 32.94 (h), 32.75 k), 32.58 (j), 25.83 (r), 25.65 (o), 19.61 (m), 17.77 (s)
IR (neat)	3271 (N-H stretch, O-H stretch), 2912, 2851, 1651 (C=O stretch), 1616, 1538 1453, 727, 694 cm^{-1}
HRMS (ESI)	$C_{21}H_{33}NNaO_2$ (M+Na): 354.2409, found 354.2412 *m/z*

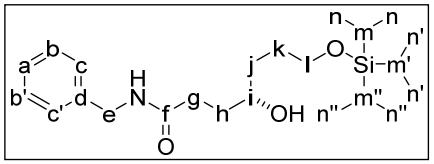
^{1}H NMR of (4*R*,7*S*)-7j



^{13}C NMR of (4*R*,7*S*)-7j

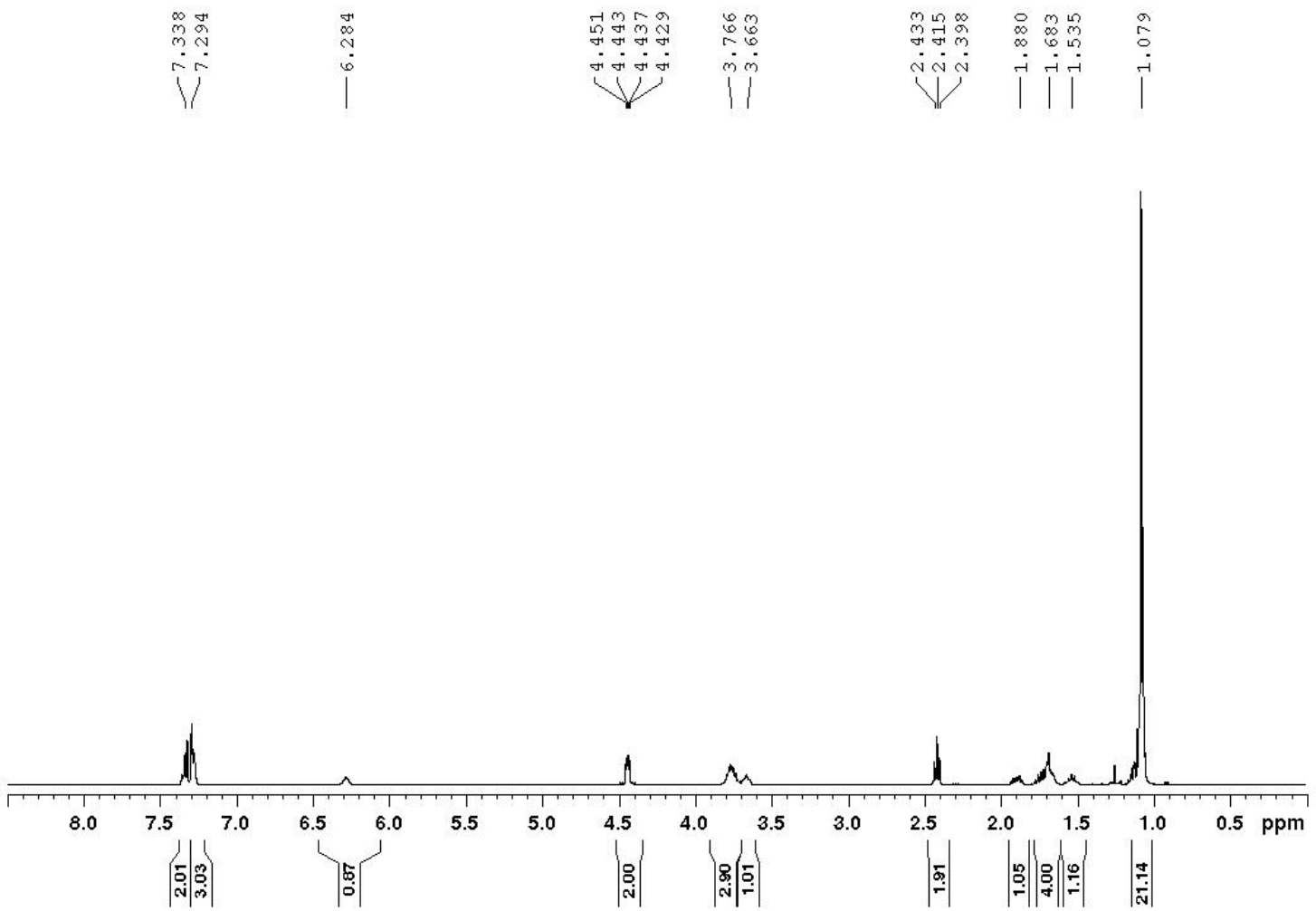




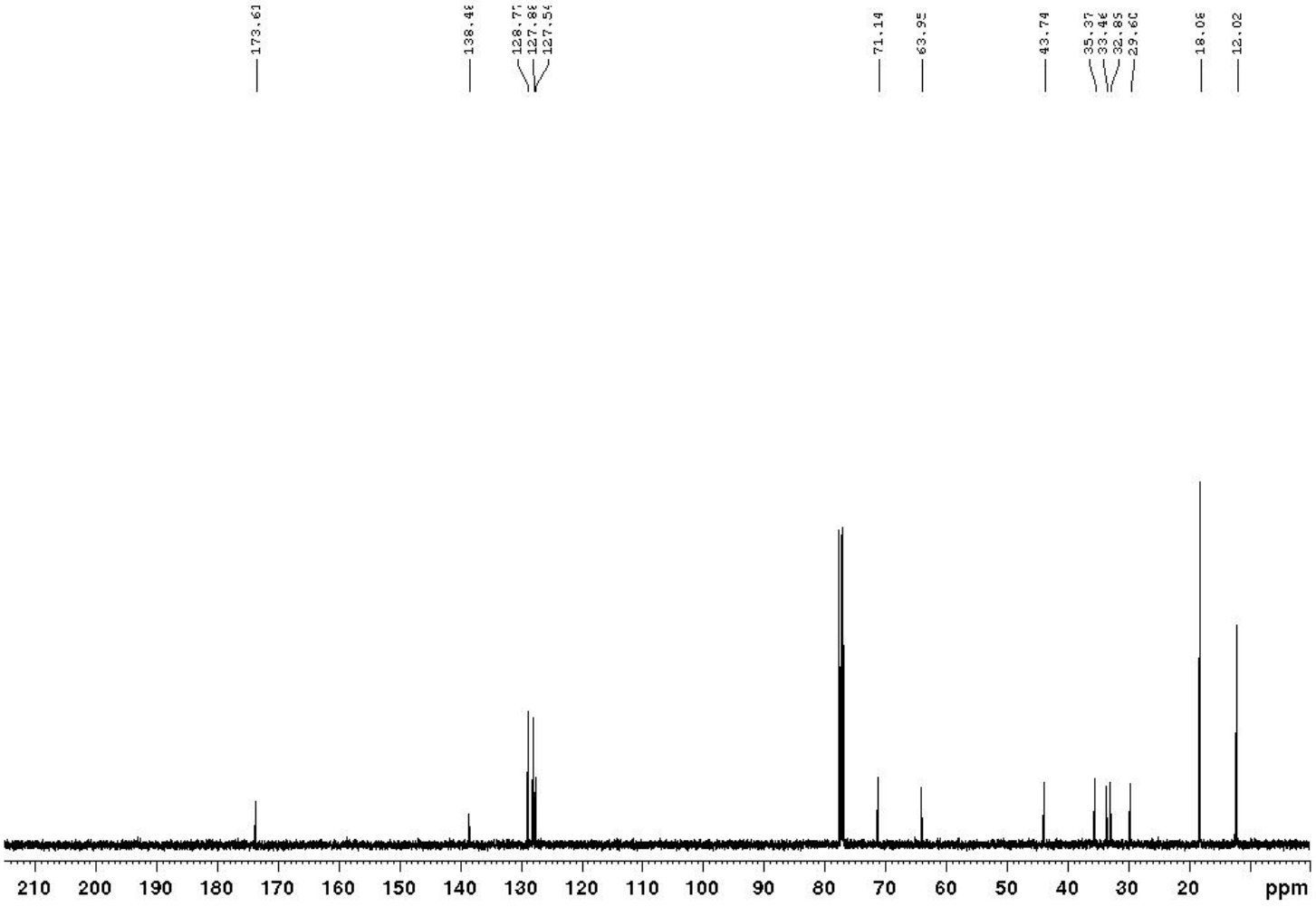


$[\alpha]_D^{20}$	+7.1° (*c* 2.0, $CHCl_3$)
TLC analysis	R_f 0.4 (20:80 hexanes:ethyl acetate)
HPLC analysis	Chiral HPLC analysis (Chiralpak-IC, 80:20 hexanes:isopropanol, flowrate = 1.4 mL/min) showed peaks at 29 minutes (3.0% (*R*)) and 35 minutes (97.0% (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.35 (2H, b,b'), 7.25–7.30 (3H, a,c,c'), 6.28 (1H, br s, NH), 4.44 (2H, dd, *J* = 5.6 and 3.2 Hz, e), 3.70–3.85 (3H, m, l, OH), 3.60–3.70 (1H, m, i), 2.42 (2H, t, *J* = 7.0 Hz, g), 1.85–1.95 (1H, m, h), 1.60–1.80 (4H, m, h,j,k), 1.50–1.60 (1H, m, j), 1.00–1.15 (3H, m, m,m',m'', *overlapping with* n,n',n''), 1.08 (18H, s, n,n',n'')
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.61 (f), 138.48 (d), 128.77 (b,b'), 127.88 (c,c'), 127.54 (a), 71.14 (i), 63.95 (l), 43.74 (e), 35.37 (j), 33.46 (g), 32.89 (h), 29.60 (k), 18.08 (n,n',n''), 12.02 (m,m',m'')
IR (neat)	3289 (N-H stretch, O-H stretch), 2941, 2864, 1644 (C=O stretch), 1548, 1454, 1097, 881, 679 cm^{-1}
HRMS (ESI)	$C_{23}H_{41}NNaO_3Si$ (M+Na): 430.2753, found 430.2763 *m/z*

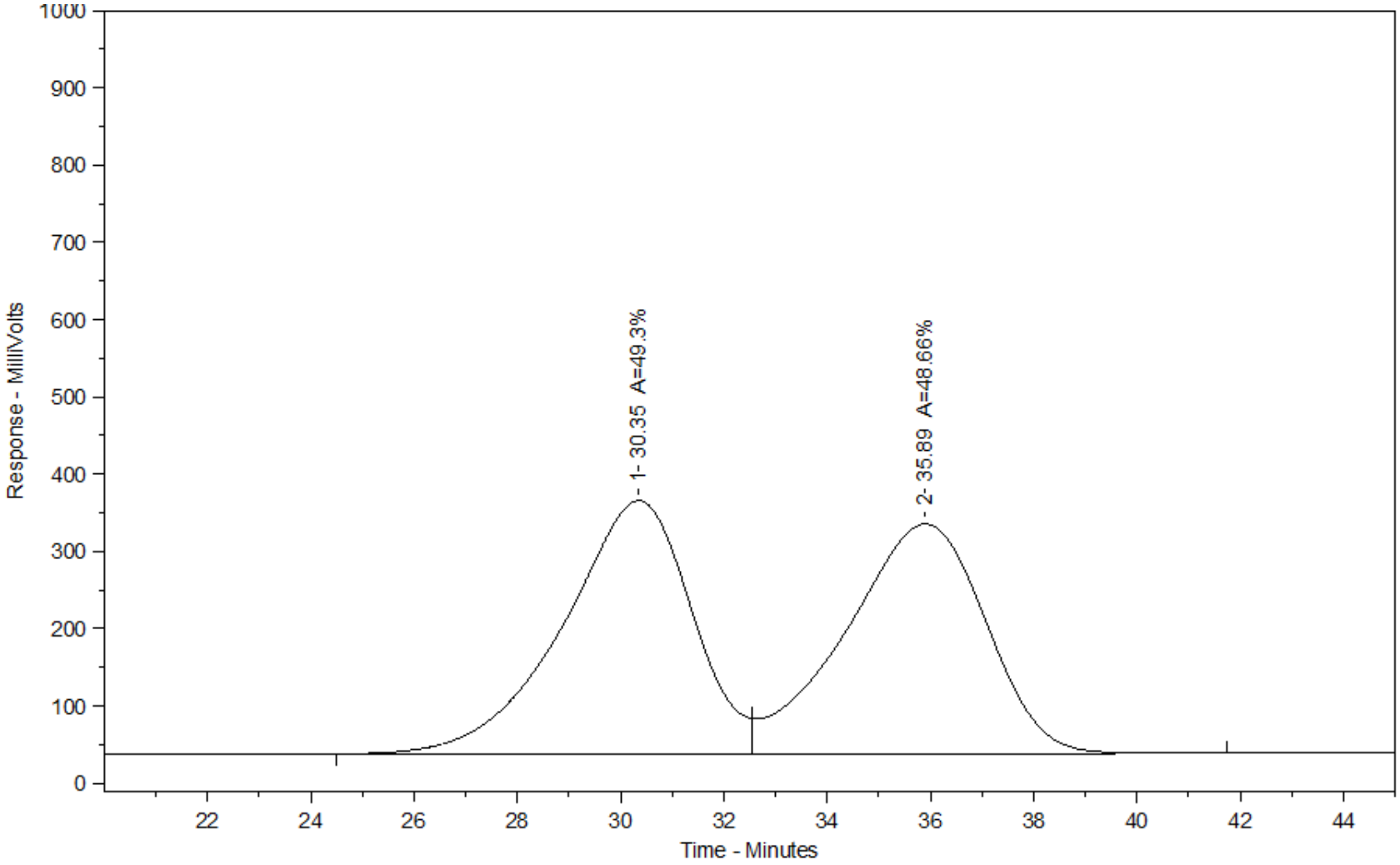
^{1}H NMR of 7k


7.338
7.294
6.284
4.451
4.443
4.437
4.429
3.766
3.663
2.433
2.415
2.398
1.880
1.683
1.535
1.079
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.01
3.03
0.87
2.00
2.90
1.01
1.91
1.05
4.00
1.16
21.14

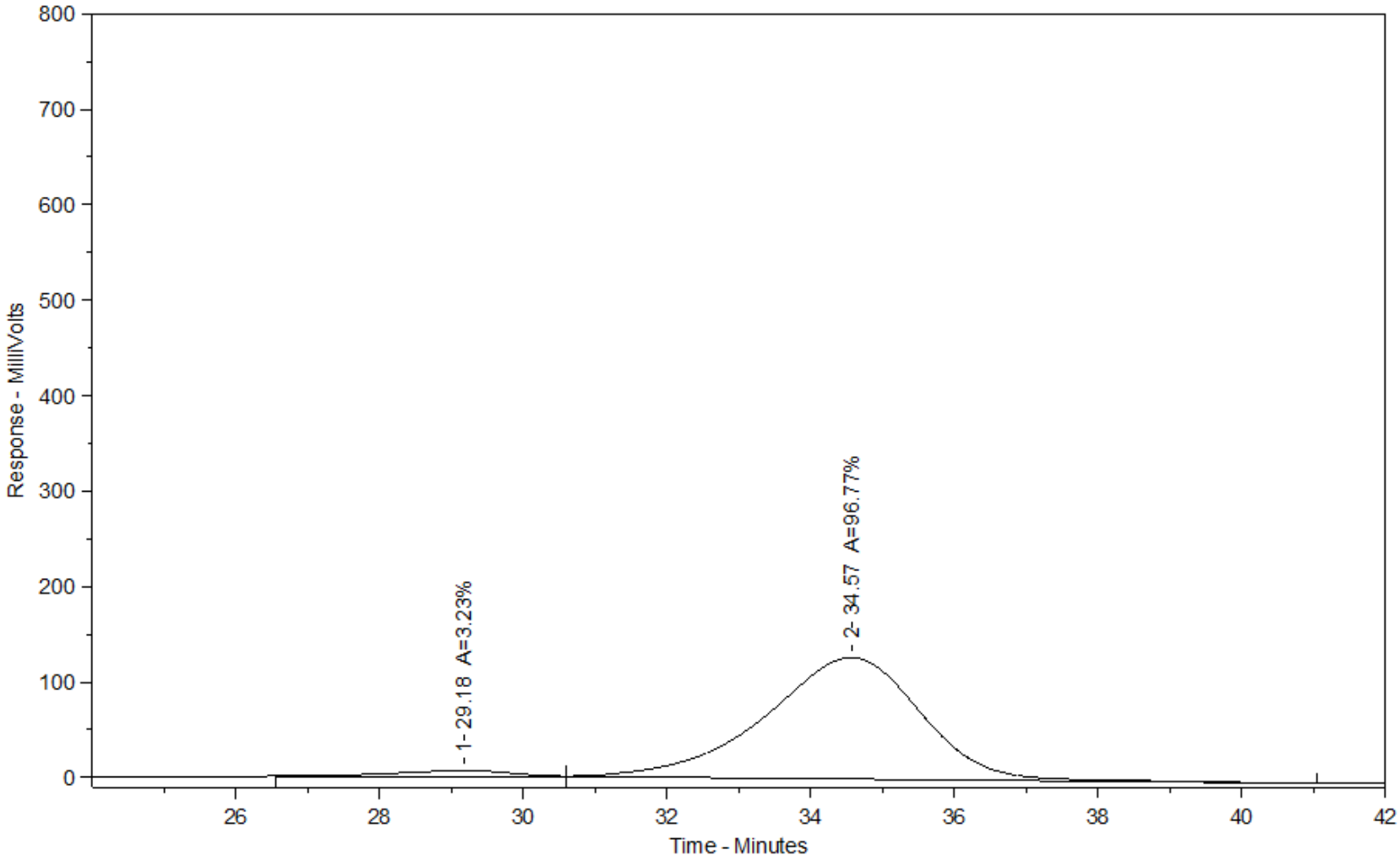
^{13}C NMR of 7k


173.61
138.46
128.77
127.88
127.54
71.14
63.95
43.74
35.37
33.46
32.85
29.60
18.06
12.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

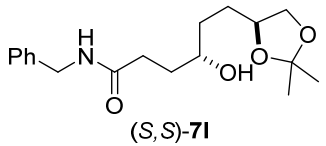
HPLC trace of 7k



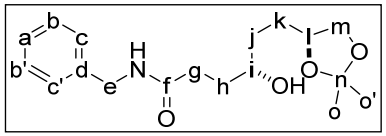
Racemic **7k**


800
700
600
500
400
300
200
100
0
Response - MilliVolts
- 1- 29.18 A=3.23%
- 2- 34.57 A=96.77%
26
28
30
32
34
36
38
40
42
Time - Minutes

(*S*)-**7k**

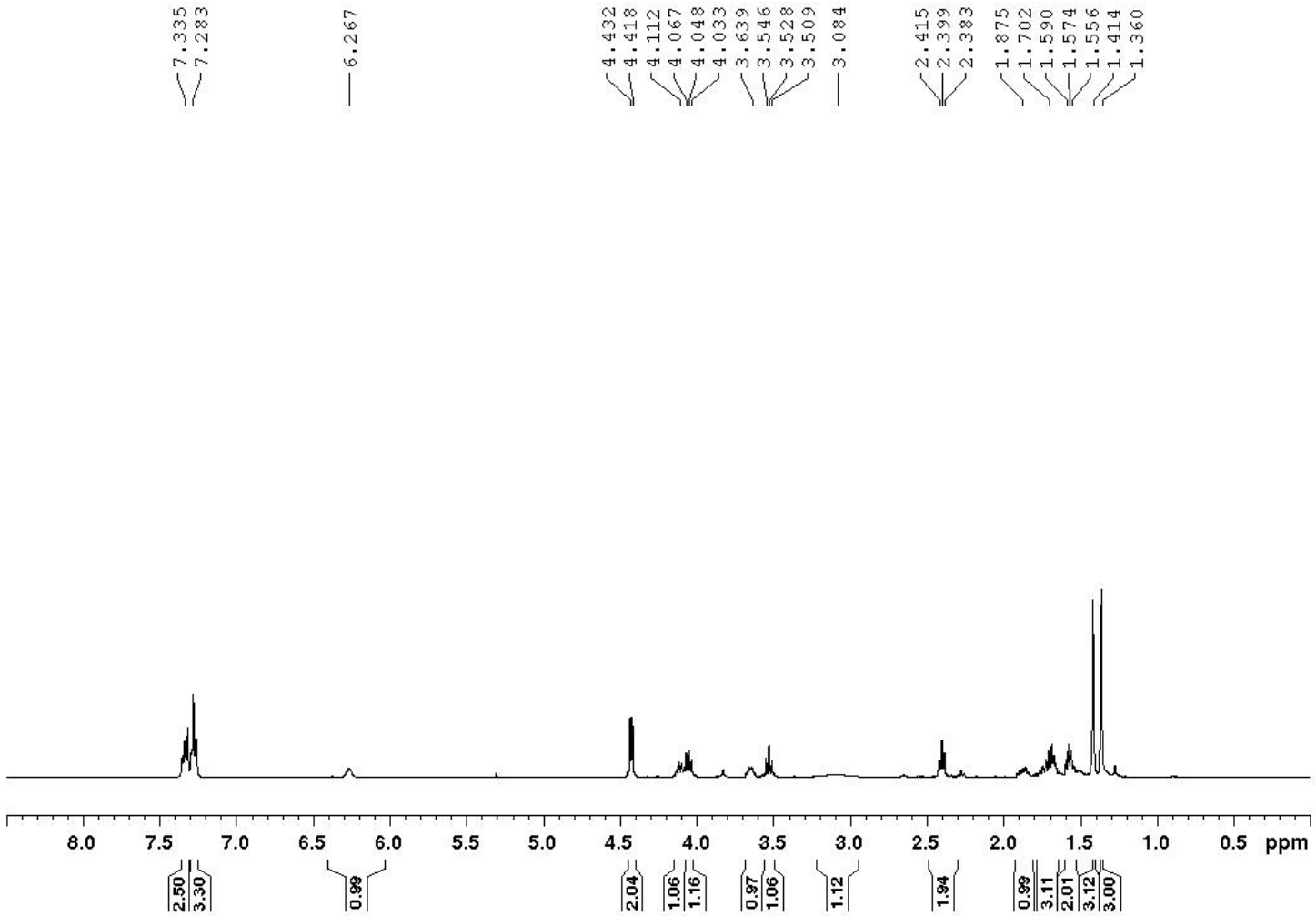


(*S*,*S*)-**7l**

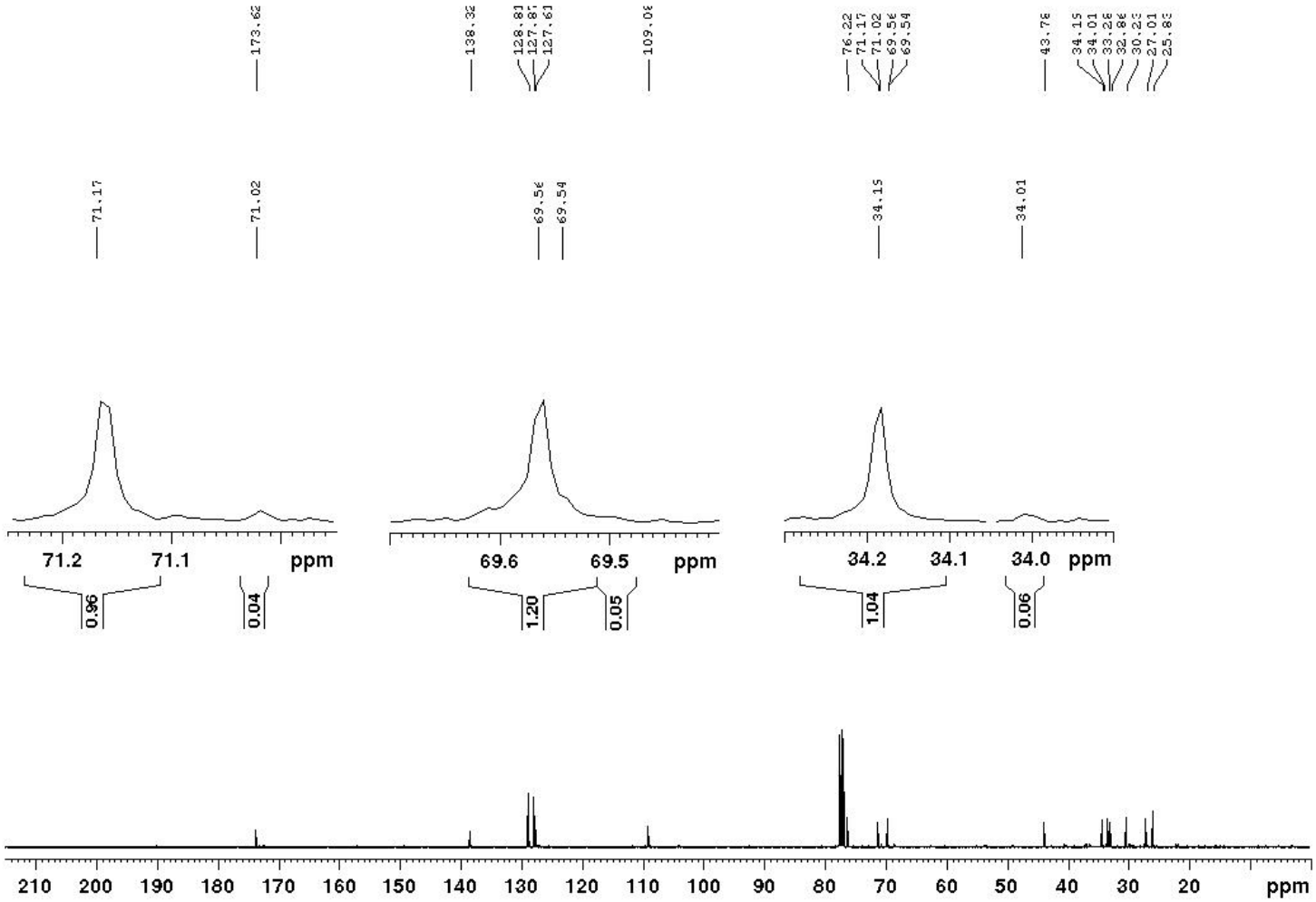


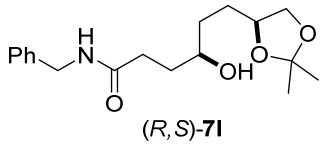
$[\alpha]_D^{20}$	+10.1° (*c* 1.0, $CHCl_3$)
TLC analysis	R_f 0.25 (0:100 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.35 (2H, m, b,b'), 7.25–7.30 (3H, m, a,c,c'), 6.27 (1H, br s, NH), 4.42 (2H, d, *J* = 5.7 Hz, e), 4.05–4.15 (1H, m, l), 4.05 (1H, dd, *J* = 6.0 and 6.0 Hz, m), 3.60–3.70 (1H, m, i), 3.53 (1H, dd, *J* = 7.5 and 7.5 Hz, m), 3.08 (1H. br s, OH), 2.40 (2H, t, *J* = 6.6 Hz, g), 1.80–1.90 (1H, m, h), 1.60–1.80 (3H, m, h,k), 1.50–1.60 (2H, m, j), 1.41 (3H, s, o,o'), 1.36 (3H, s, o,o')
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.62 (f), 138.32 (d), 128.81 (b,b'), 127.87 (c,c'), 127.61 (a), 109.08 (n), 76.22 (l), 71.17 (major diastereomer, 96%, i), 71.02 (minor diastereomer, 4%, i), 69.56 (major diastereomer, 96%, m), 69.54 (minor diastereomer, 4%, m), 43.78 (e), 34.19 (major diastereomer, 95%, j), 34.01 (minor diastereomer, 5%, j), 33.28 (g), 32.86 (h), 30.23 (k), 27.01 (o,o'), 25.83 (o,o')
IR (neat)	3298 (N-H stretch, O-H stretch), 2984, 2932, 2868, 1644 (C=O stretch), 1543, 1454, 1369, 1214, 1155, 1053, 698 cm^{-1}
HRMS (ESI)	$C_{18}H_{27}NNaO_4$ (M+Na): 344.1838, found 344.1847 *m/z*

^{1}H NMR of (*S*,*S*)-7l

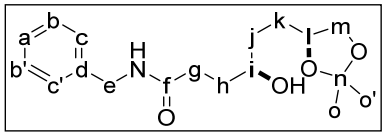


^{13}C NMR of (*S*,*S*)-7l



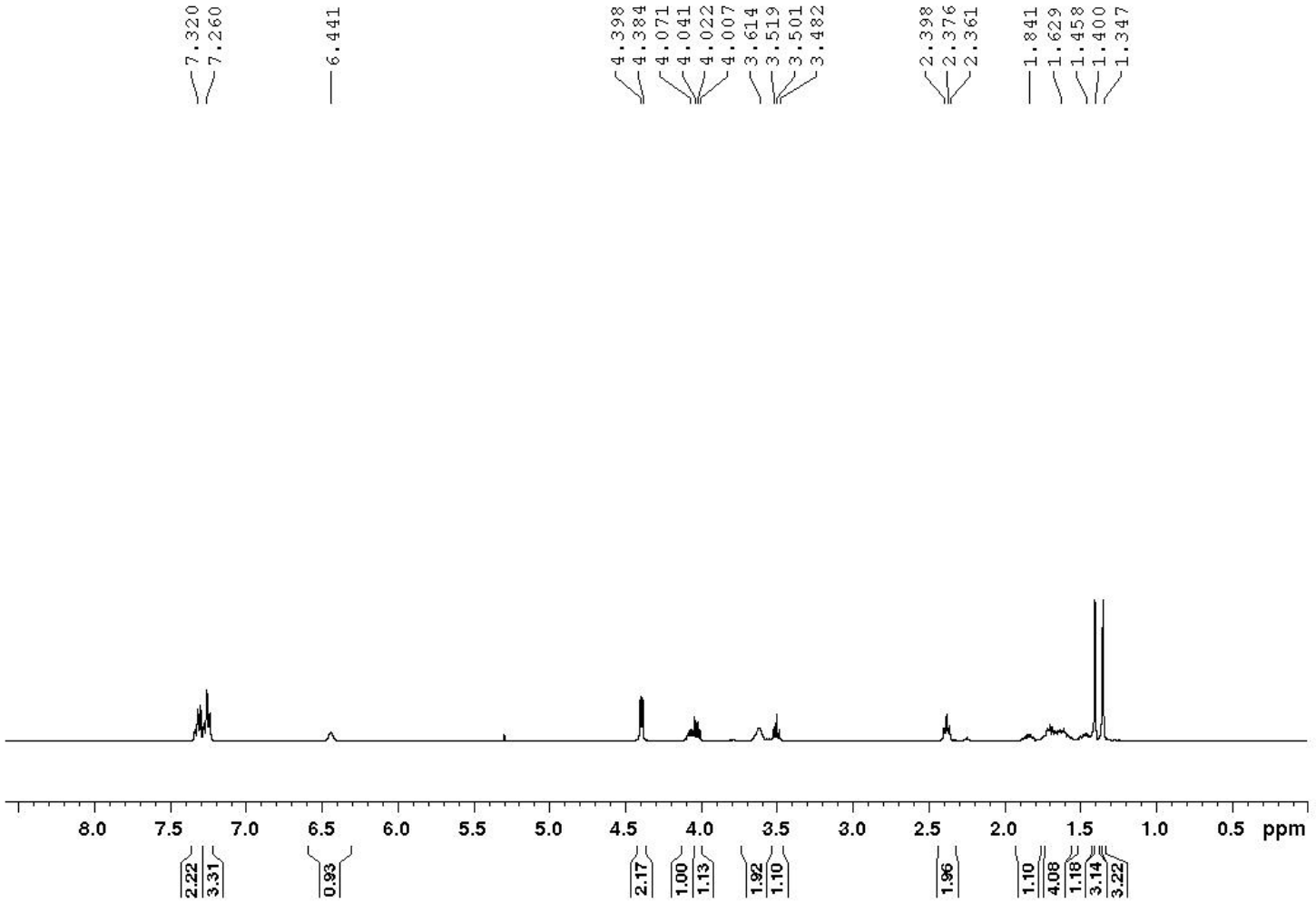


(*R*,*S*)-**7l**

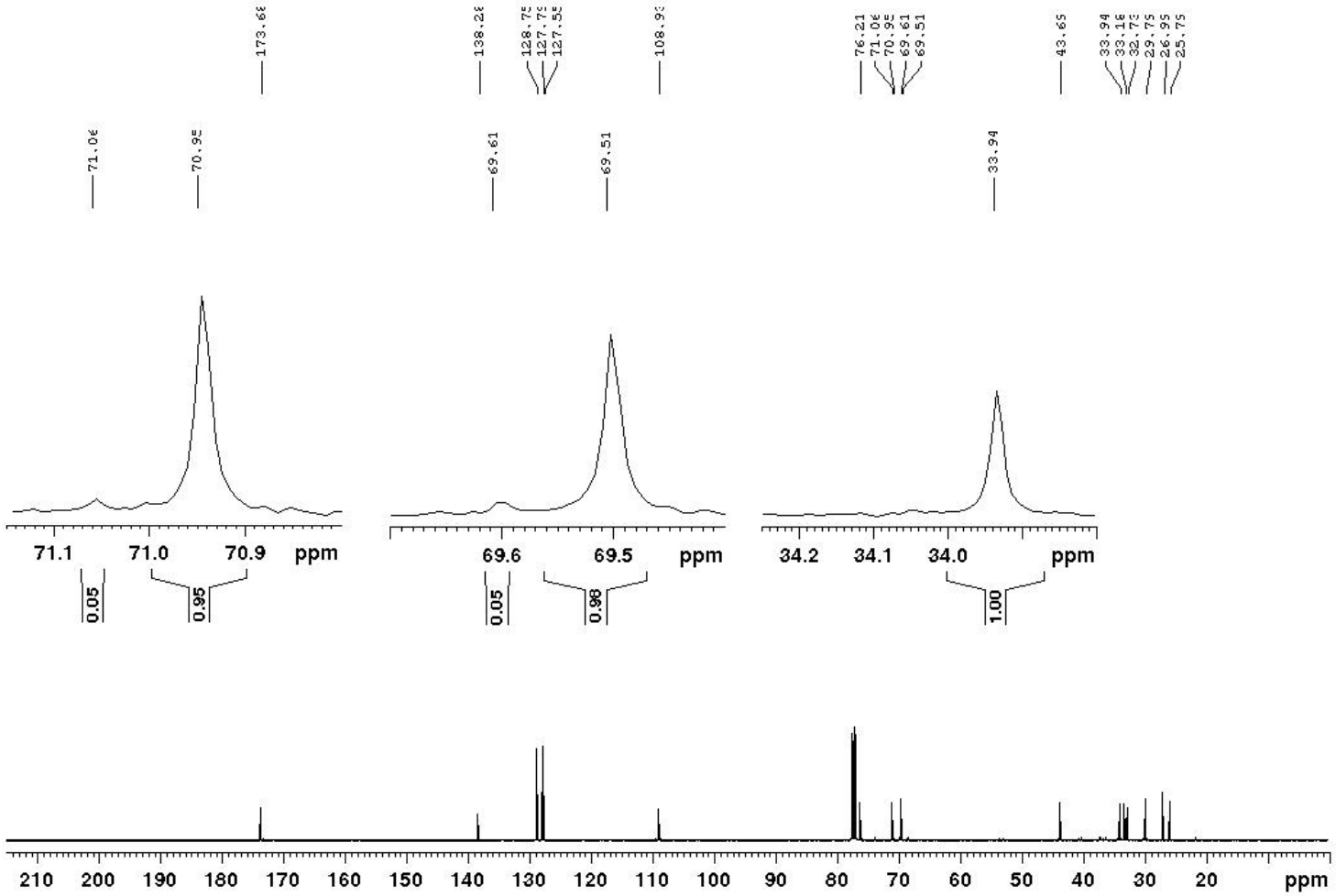


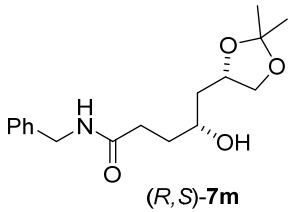
$[\alpha]_D^{20}$	+22.3° (*c* 1.0, $CHCl_3$)
TLC analysis	R_f 0.25 (0:100 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.35 (2H, m, b,b'), 7.20–7.30 (3H, m, a,c,c'), 6.44 (1H, br s, NH), 4.39 (2H, d, *J* = 5.7 Hz, e), 4.05–4.15 (1H, m, l), 4.02 (1H, dd, *J* = 7.6 and 7.6 Hz, m), 3.55–3.75 (2H, m, i, OH), 3.50 (1H, dd, *J* = 7.2 and 7.2 Hz, m), 2.36 (1H, t, *J* = 6.0 Hz, g), 1.80–1.90 (1H, m, h), 1.55–1.80 (4H, m, h,j,k), 1.45–1.50 (1H, m, j), 1.40 (3H, s, o,o'), 1.35 (3H, s, o,o')
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.68 (f), 138.28 (d), 128.75 (b,b'), 127.79 (c,c'), 127.55 (a), 108.93 (n), 76.21 (l), 71.06 (minor diastereomer, 5%, i), 70.95 (major diastereomer, 95%, i), 69.61 (minor diastereomer, 5%, m), 69.51 (major diastereomer, 95%, m), 43.69 (e), 34.19 (minor diastereomer, 0%, j), 33.94 (major diastereomer, 100%, j), 33.18 (g), 32.73 (h), 29.79 (k), 26.99 (o,o'), 25.79 (o,o')
IR (neat)	3294 (N-H stretch, O-H stretch), 2984, 2931, 2869, 1644 (C=O stretch), 1542, 1454, 1369, 1214, 1054, 698 cm^{-1}
HRMS (ESI)	$C_{18}H_{27}NNaO_4$ (M+Na): 344.1838, found 344.1851 *m/z*

^{1}H NMR of (*R*,*S*)-7l

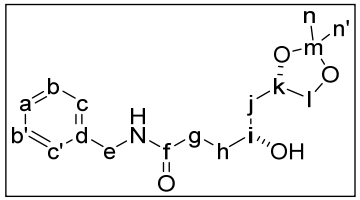


^{13}C NMR of (*R*,*S*)-7l



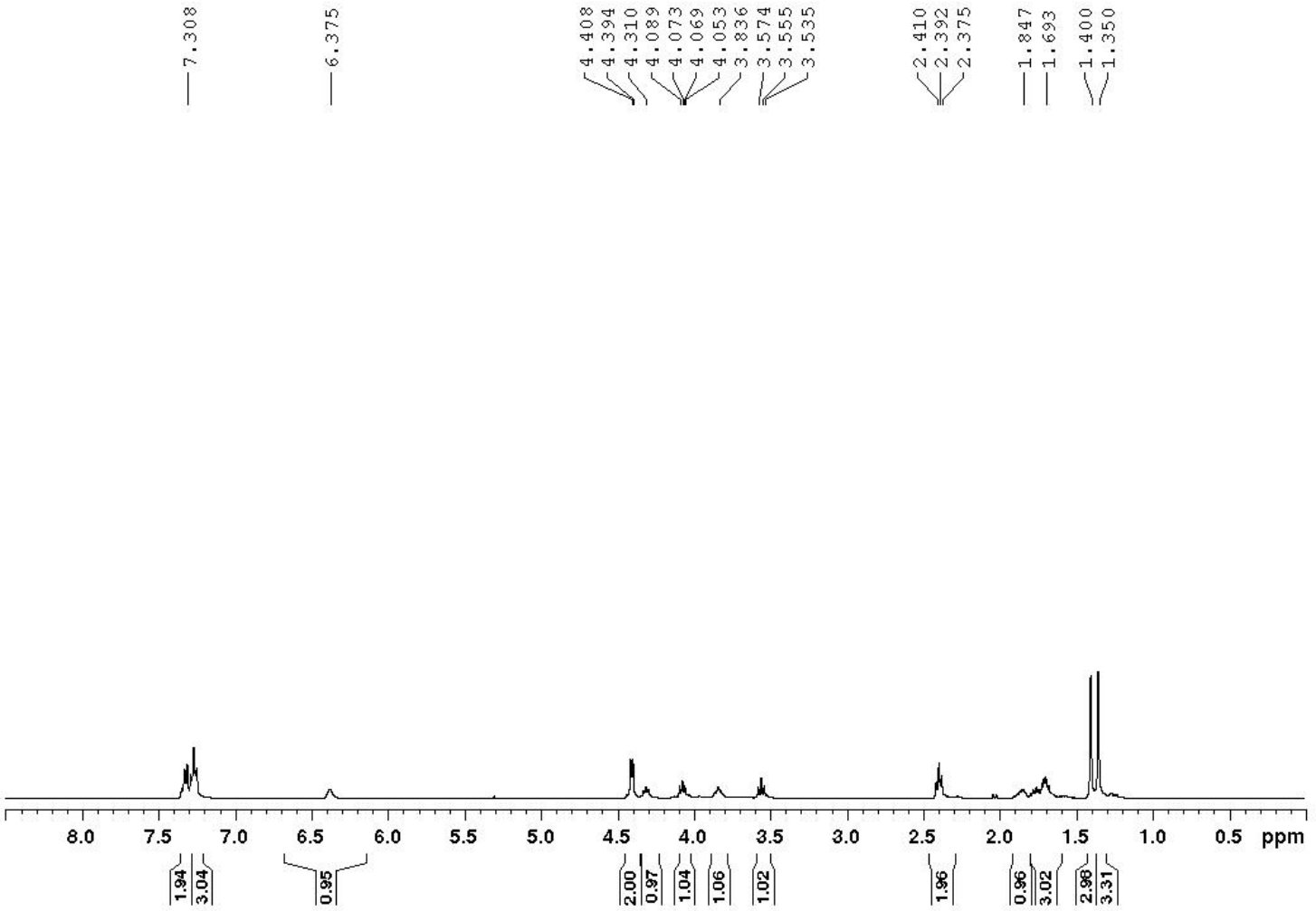


(*R,S*)-**7m**

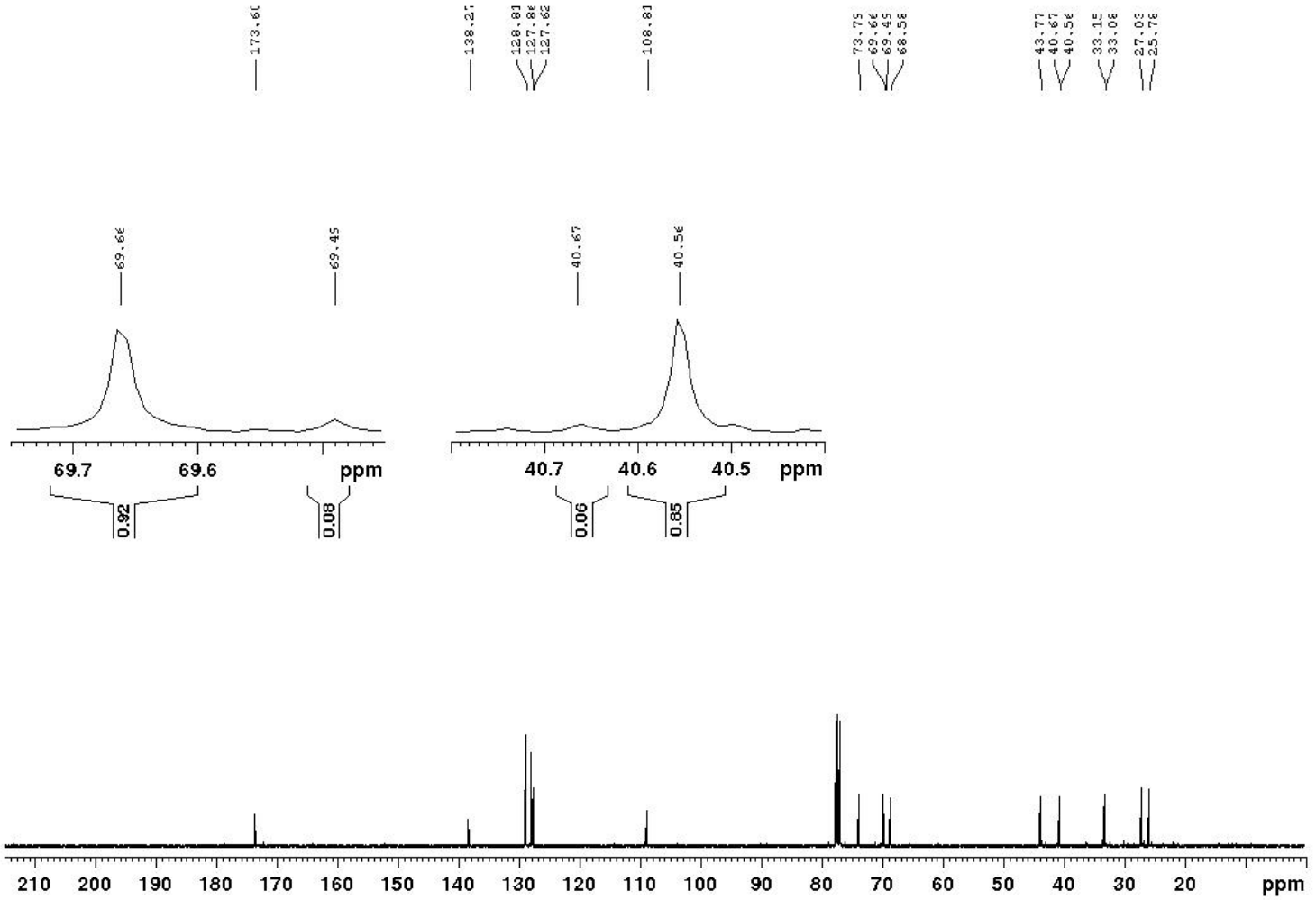


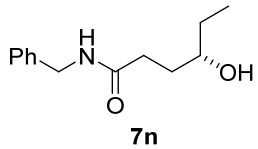
$[\alpha]_D^{20}$	–3.5° (*c* 1.0, $CHCl_3$)
TLC analysis	R_f 0.25 (0:100 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.30–7.35 (2H, m, b,b'), 7.20–7.30 (3H, m, a,c,c'), 6.37 (1H, br s, NH), 4.40 (2H, d, *J* = 5.7 Hz, e), 4.25–4.35 (1H, m, k), 4.07 (1H, dd, *J* = 8.0 and 6.1 Hz, l), 3.80–3.90 (1H, m, i), 3.55 (1H, dd, *J* = 7.8 and 7.8 Hz, l), 2.39 (1H, t, *J* = 6.9 Hz, g), 1.80–1.90 (1H, m, h), 1.60–1.80 (3H, m, h,j), 1.40 (3H, s, n,n'), 1.35 (3H, s, n,n')
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.60 (f), 138.27 (d), 128.81 (b,b'), 127.86 (c,c'), 127.62 (a), 108.81 (m), 73.79 (k), 69.66 (major diastereomer, 92%, i), 69.49 (minor diastereomer, 8%, i), 68.58 (l), 43.77 (e), 40.67 (minor diastereomer, 7%, j), 40.56 (major diastereomer, 93%, j), 33.15 (g), 33.08 (h), 27.03 (n,n'), 25.78 (n,n')
IR (neat)	3304 (N-H stretch, O-H stretch), 2984, 2935, 2873, 1644 (C=O stretch), 1542, 1454, 1369, 1214, 1155, 1052, 698 cm^{-1}
HRMS (ESI)	$C_{17}H_{25}NNaO_4$ (M+Na): 330.1681, found 330.1690 *m/z*

^{1}H NMR of (*R*,*S*)-7m

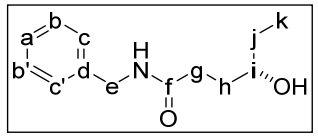


^{13}C NMR of (*R*,*S*)-7m



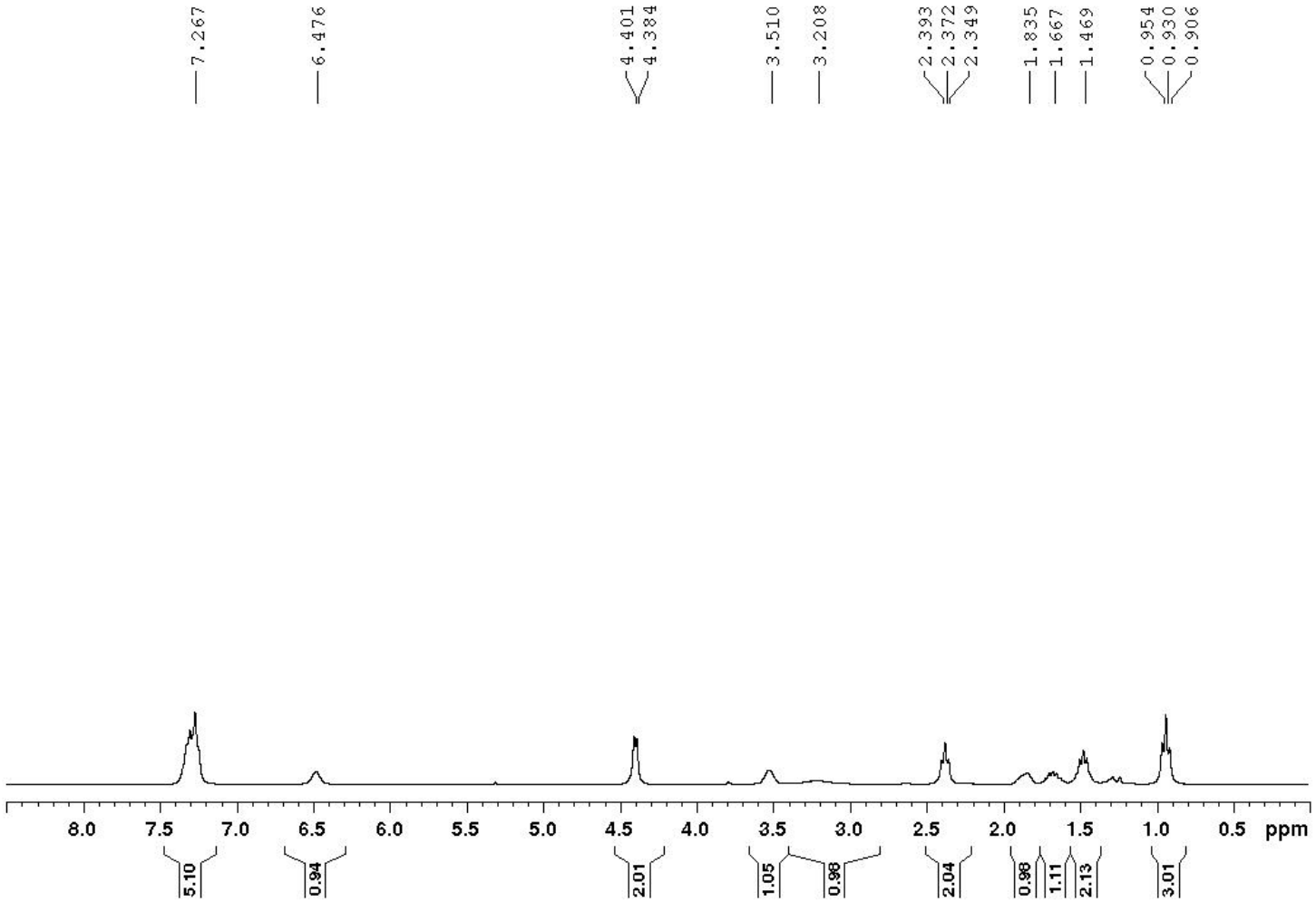


7n



$[\alpha]_D^{20}$	+5.3° (*c* 1.44, $CHCl_3$)
m.p.	63.5–64.5 °C;
TLC analysis	R_f 0.4 (0:100 hexanes:ethyl acetate)
^{1}H NMR (300 MHz, $CDCl_3$)	δ 7.20–7.40 (5H, a,b,b',c,c'), 6.48 (1H, br s, NH), 4.40 (2H, d, *J* = 5.2 Hz, e), 3.40–3.60 (1H, m, i), 3.21 (1H, br s, OH), 2.37 (2H, t, *J* = 6.5 Hz, g) 1.75–1.95 (1H, m, h), 1.55–1.75 (1H, m, h), 1.40–1.55 (2H, m, j), 0.93 (3H, t, *J* = 7.2 Hz, k)
^{13}C NMR (75 MHz, $CDCl_3$)	δ 173.80 (f), 138.24 (d), 128.67 (b,b'), 127.74 (c,c'), 127.46 (a), 72.67 (i), 43.62 (e), 33.12 (g), 32.16 (h), 30.40 (j), 10.02 (k)
IR (neat)	3280 (N-H stretch, O-H stretch), 2964, 2920, 2877, 1631 (C=O stretch), 1549 (N-H bend), 1493, 1326, 1264, 936, 729, 693 cm^{-1}
HRMS (ESI)	$C_{13}H_{19}NNaO_2$ (M+Na): 244.1313, found 244.1316 *m/z*

^{1}H NMR of 7n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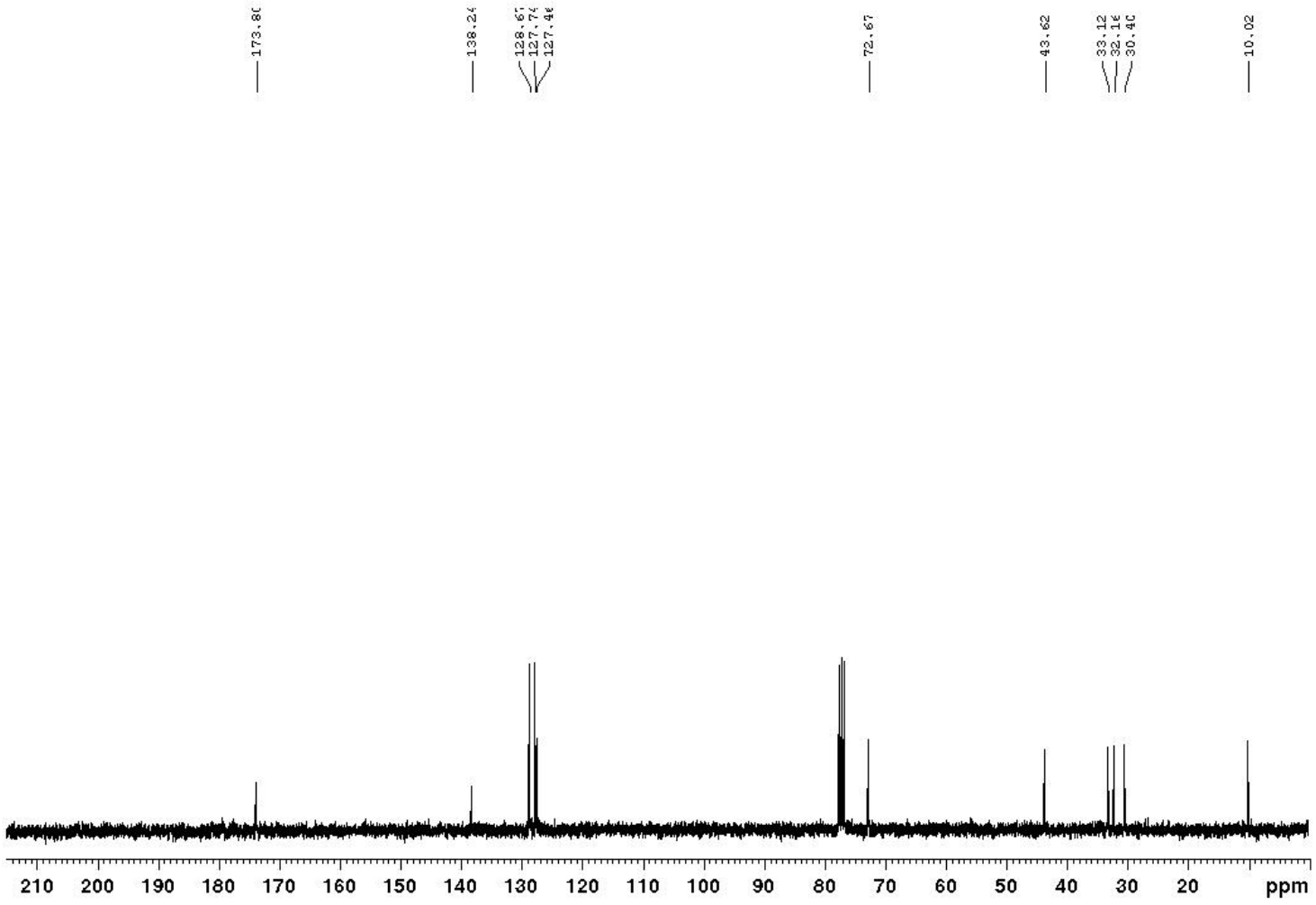
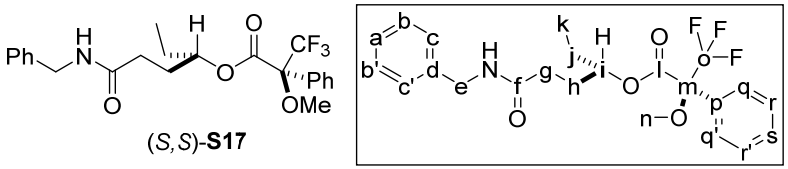
0.930
0.906
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.10
0.94
2.01
1.05
0.96
2.04
0.98
1.11
2.13
3.01

^{13}C NMR of 7n

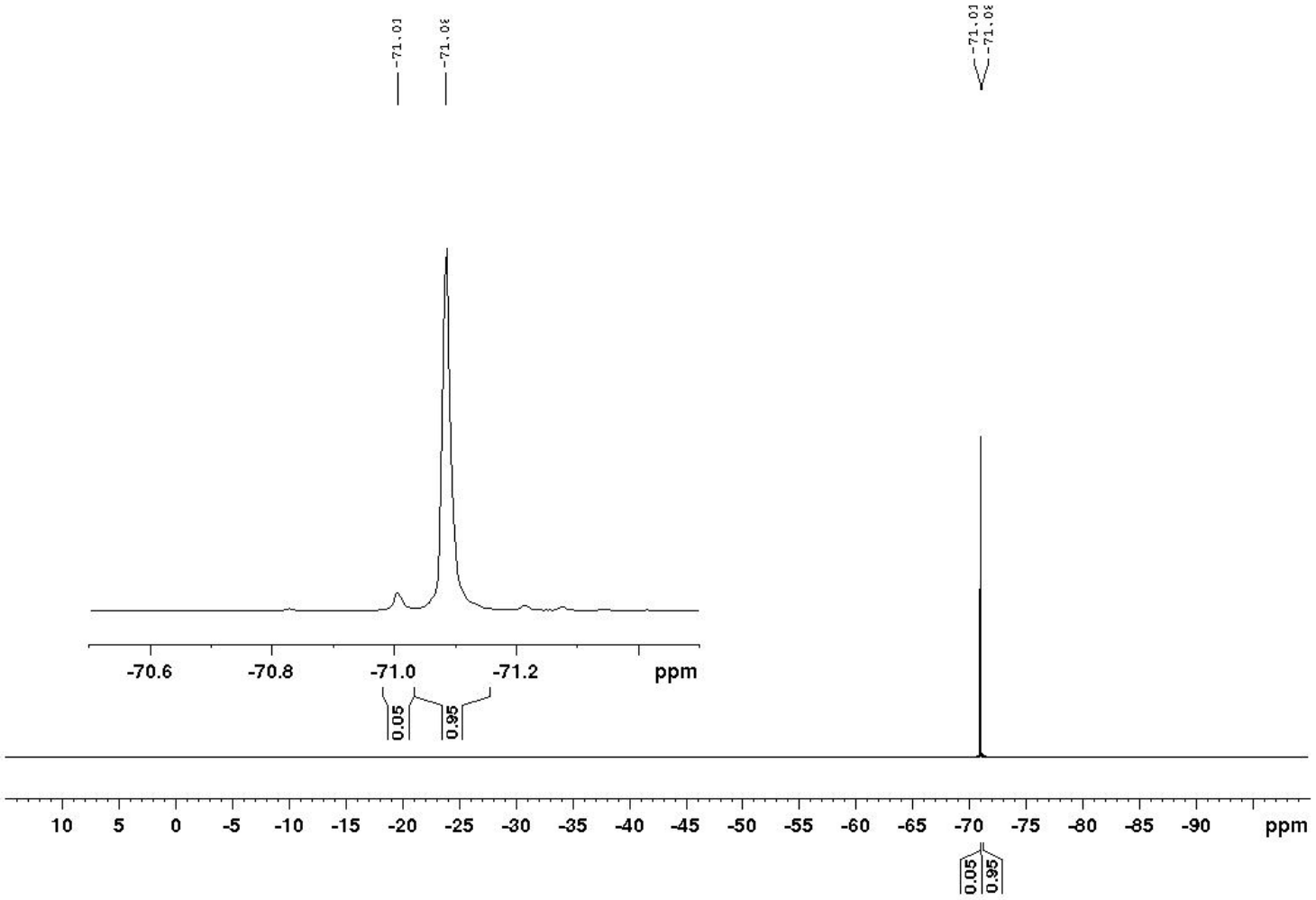

173.80
138.24
128.67
127.74
127.48
72.67
43.62
33.12
32.16
30.40
10.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm



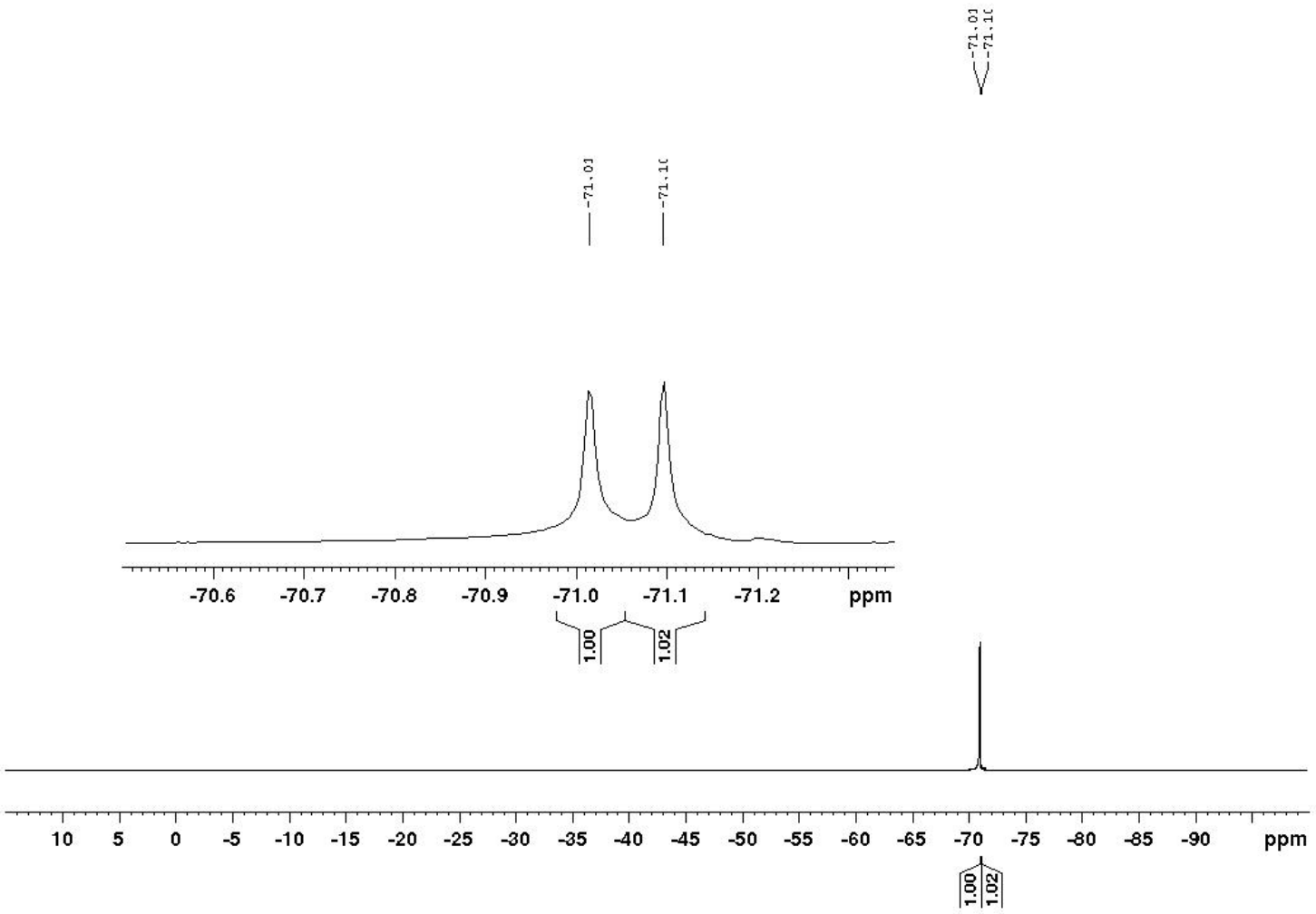
(*S,S*)-**S17**

$[\alpha]_D^{20}$	–34.5° (*c* 1.87, $CHCl_3$)
TLC analysis	R_f 0.5 (50:50 hexanes:ethyl acetate)
^{19}F NMR (376 MHz, $CDCl_3$)	δ –71.01 (s, 5%, minor, CF_3), –71.08 (s, 95%, major, CF_3)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.50–7.60 (2H, m, r,r'), 7.25–7.45 (8H, a,b,b',c,c',q,q',s), 5.74 (0.94H, br s, major NH), 5.52 (0.05H, br s, minor NH), 5.00–5.15 (1H, m, i), 4.44 (2H, d, *J* = 5.7 Hz, e), 3.54 (3H, s, n), 2.05–2.30 (3H, m, g,h), 1.95–2.05 (1H, m, h), 1.60–1.70 (2H, m, j), 0.96 (0.12H, t, *J* = 7.4 Hz, minor k), 0.86 (2.89H, t, *J* = 7.4 Hz, major k)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 171.60 (f), 166.59 (l), 138.26 (d), 132.26 (p), 129.74 (r,r'), 128.85 (b,b'), 128.57 (q,q'), 127.98 (c,c'), 127.70 (s), 127.54 (a), 123.50 (q, *J* = 287 Hz, o), 84.79 and 84.52 (m), 78.16 (i), 55.47 (n), 43.82 (e), 32.21 (g), 29.38 (h), 26.82 (j), 9.37 (k)
IR (neat)	3293 (N-H stretch), 2970, 2935, 1741 (C=O stretch), 1644 (C=O stretch), 1545 (N-H bend), 1452, 1258, 1165, 1121, 1016, 992, 715, 696 cm^{-1}
HRMS (ESI)	$C_{23}H_{26}F_3NNaO_4$ (M+Na): 460.1712, found 460.1729 *m/z*

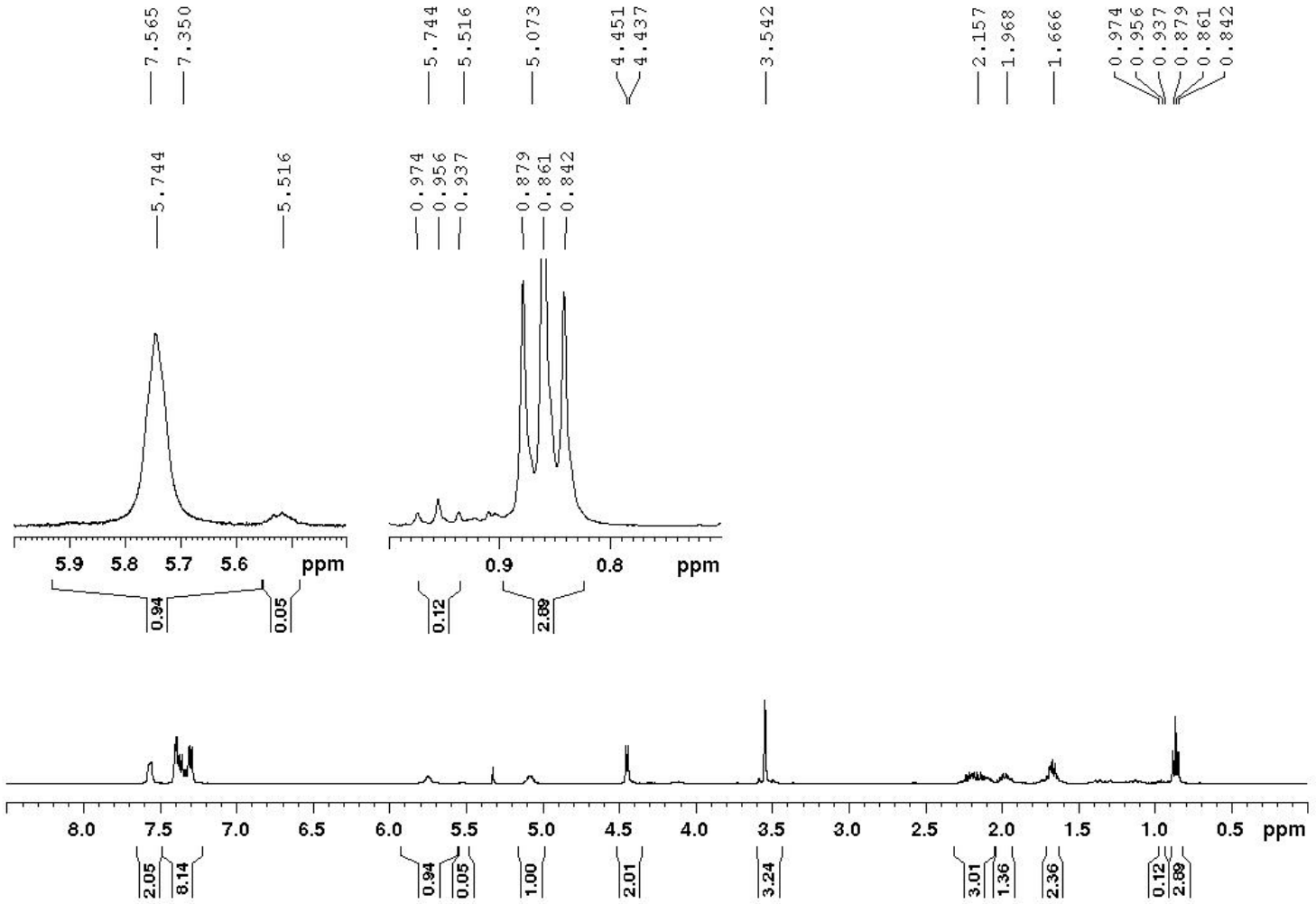
^{19}F NMR of (*S*,*S*)-S17



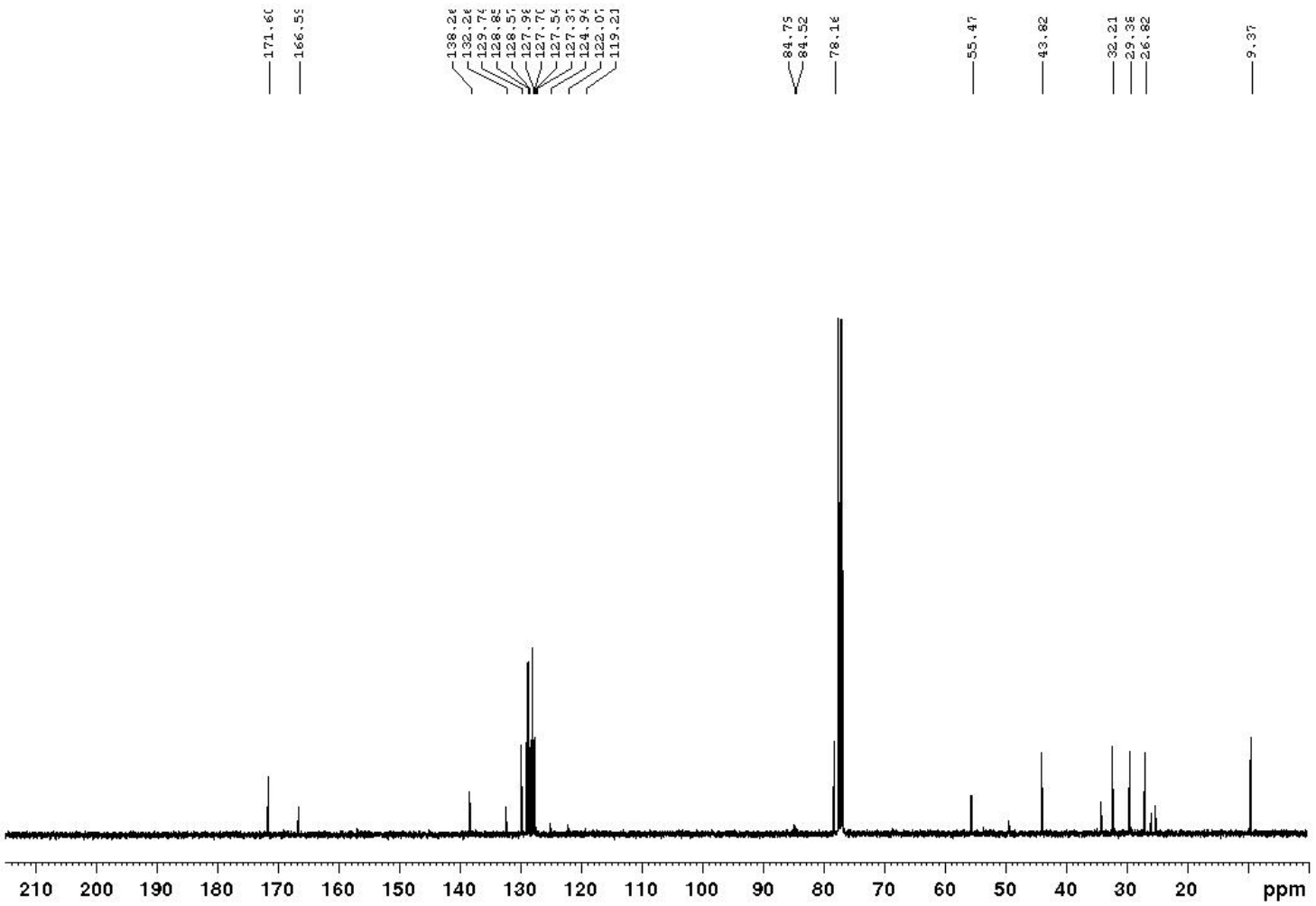
^{19}F NMR of S17 (from racemic 7n)

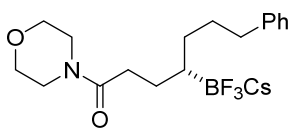


^{1}H NMR of (*S*,*S*)-S17

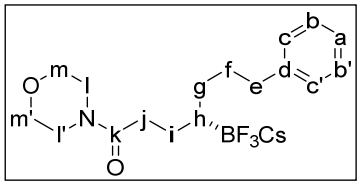


^{13}C NMR of (*S*,*S*)-S17



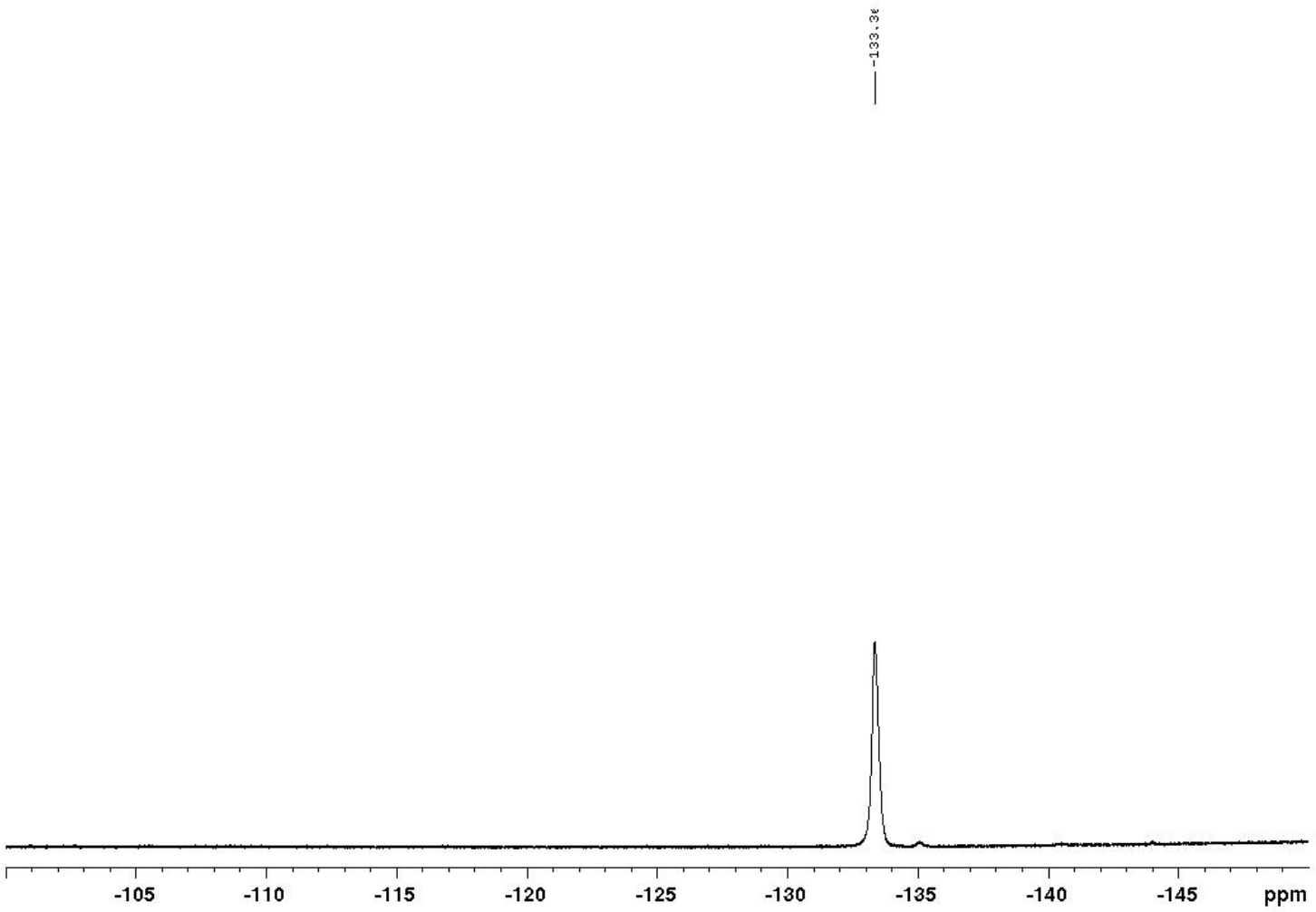


11c

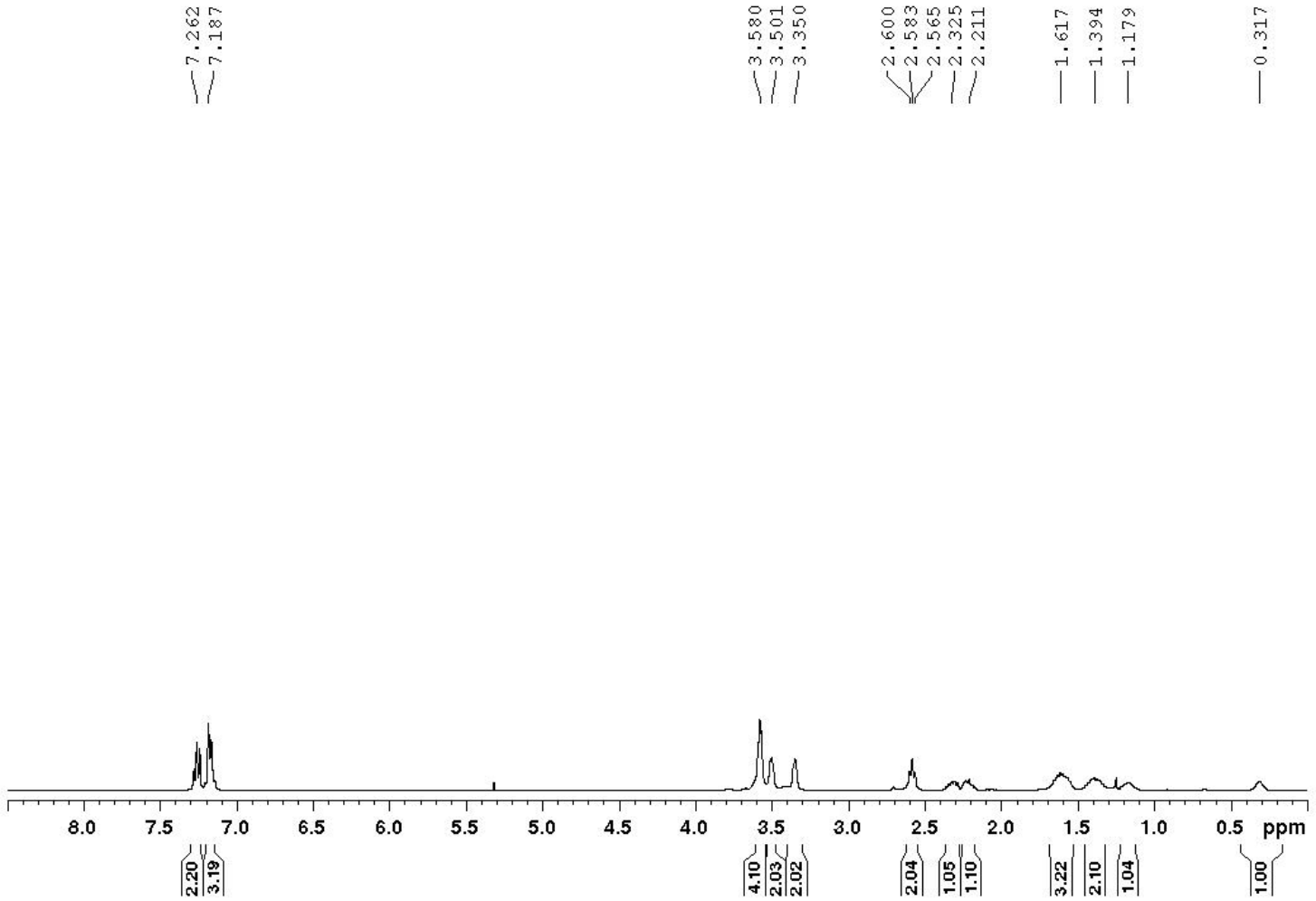


$[\alpha]_D^{20}$	+0.5° (*c* 1.0, $CHCl_3$)
m.p.	61.5–62.5 °C
^{19}F NMR (376 MHz, $CDCl_3$)	δ –133.36 (s, BF_3Cs)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.30 (2H, m, b,b'), 7.15–7.20 (3H, m, a,c,c'), 3.55–3.60 (4H, m, m,m'), 3.45–3.55 (2H, m, l,l'), 3.30–3.40 (2H, m, l,l'), 2.58 (2H, t, *J* = 6.9 Hz, e), 2.25–2.35 (1H, m, j), 2.15–2.25 (1H, m, j), 1.50–1.70 (3H, m, f,i), 1.30–1.45 (2H, m, g,i), 1.10–1.25 (1H, m, g), 0.25–0.40 (1H, m, h)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.90 (k), 143.63 (d), 128.68 (b,b'), 128.39 (c,c'), 125.64 (a), 66.94 and 66.86 (m,m'), 46.28 and 41.86 (l,l'), 36.70 (e), 31.79 (j), 31.07 (f), 30.09 (g), 26.60 (i)
IR (neat)	2908, 2854, 1609 (C=O stretch), 1461 (N-H bend), 1434, 1240 (C-N stretch), 1114, 1064, 957, 932, 742, 702 cm^{-1}
HRMS (ESI)	$C_{17}H_{24}BF_3NO_2$ (M-Cs): 342.1852, found 342.1852 *m/z*

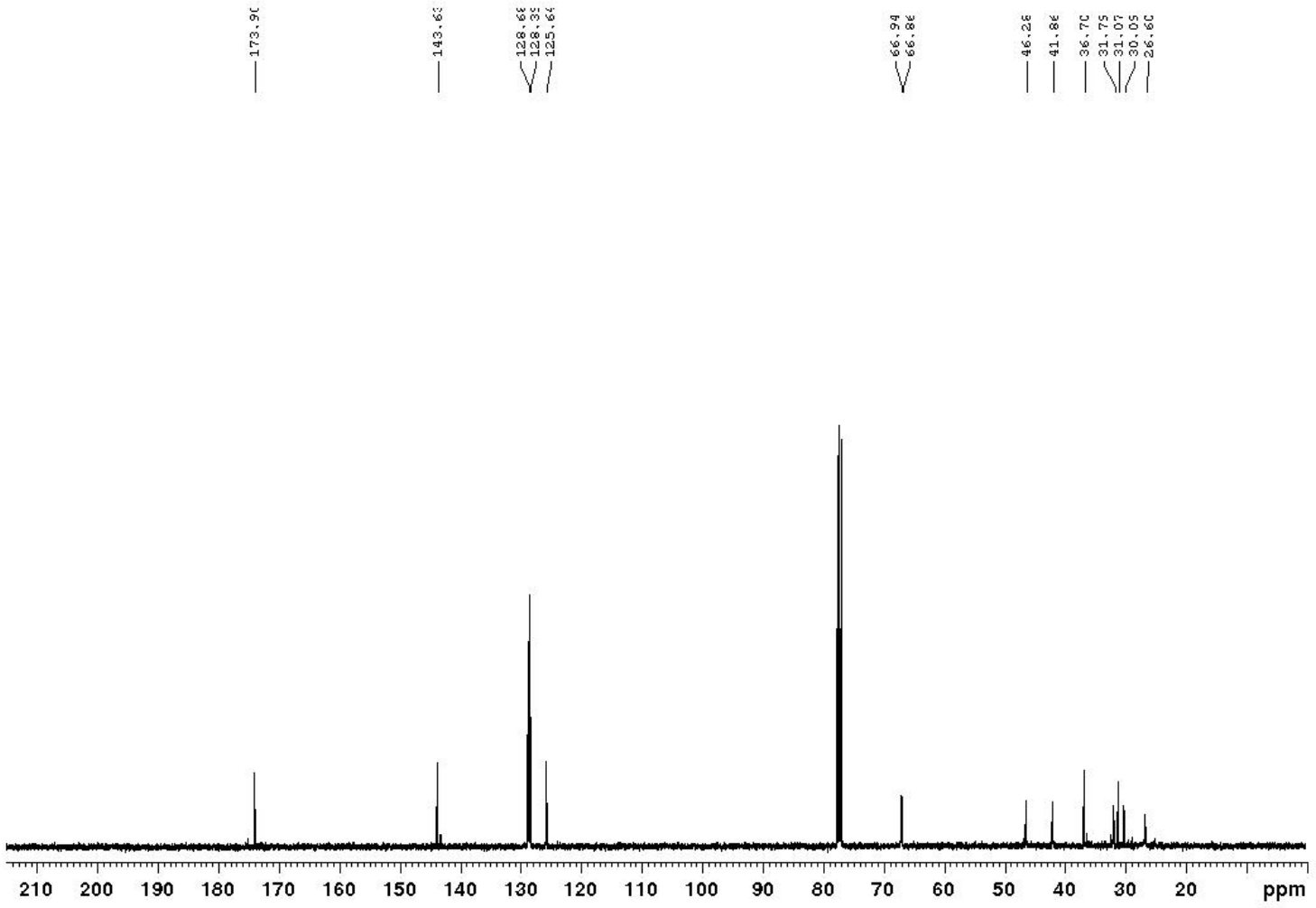
^{19}F NMR of 11c

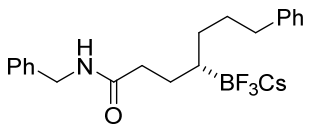


^{1}H NMR of 11c

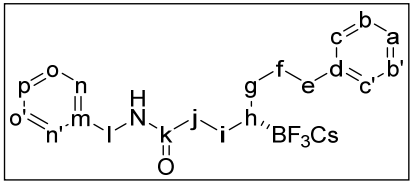

7.262
7.187
3.580
3.501
3.350
2.600
2.583
2.565
2.325
2.211
1.617
1.394
1.179
0.317
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.20
3.19
4.10
2.03
2.02
2.04
1.05
1.10
3.22
2.10
1.04
1.00

^{13}C NMR of 11c



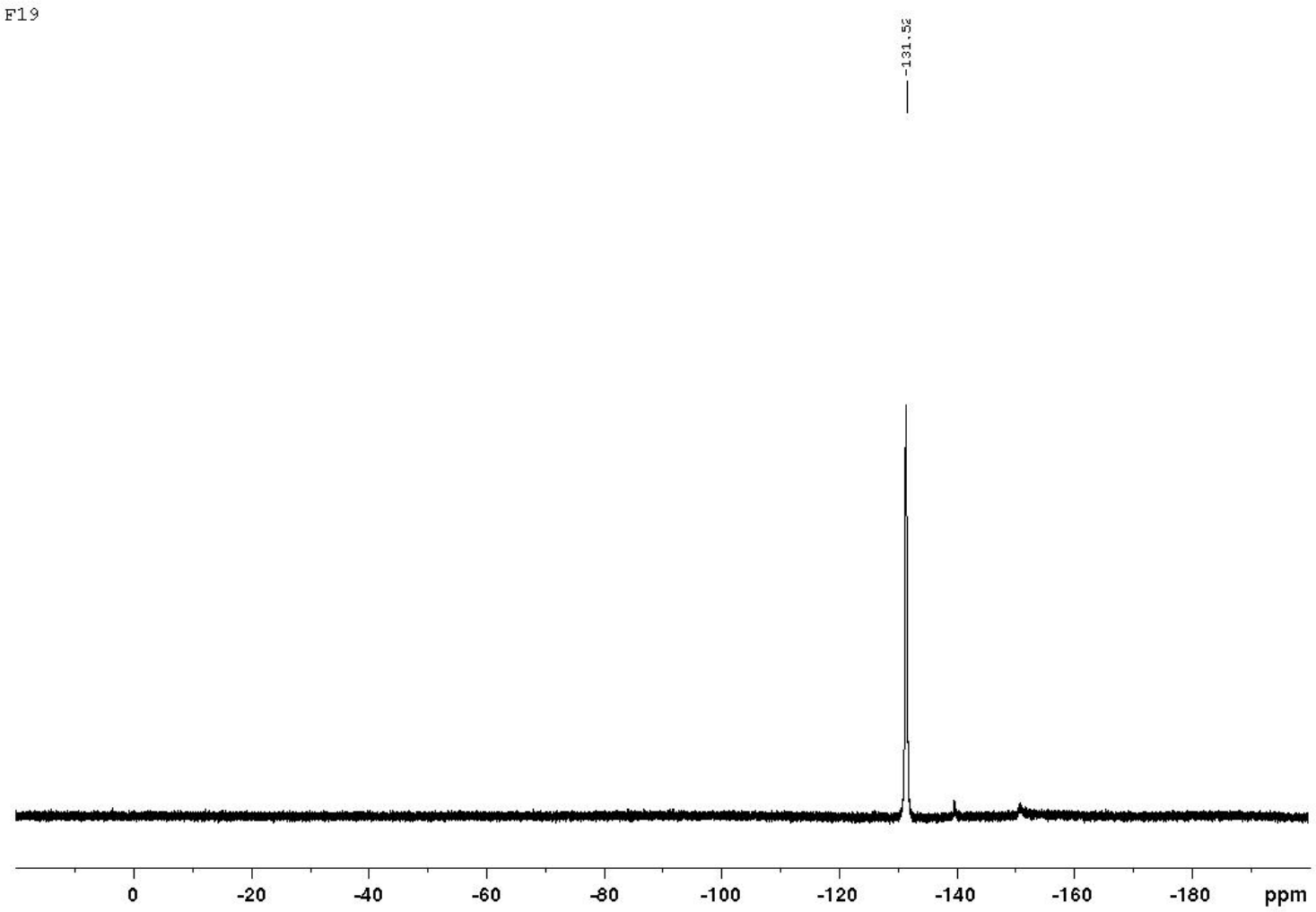


11d

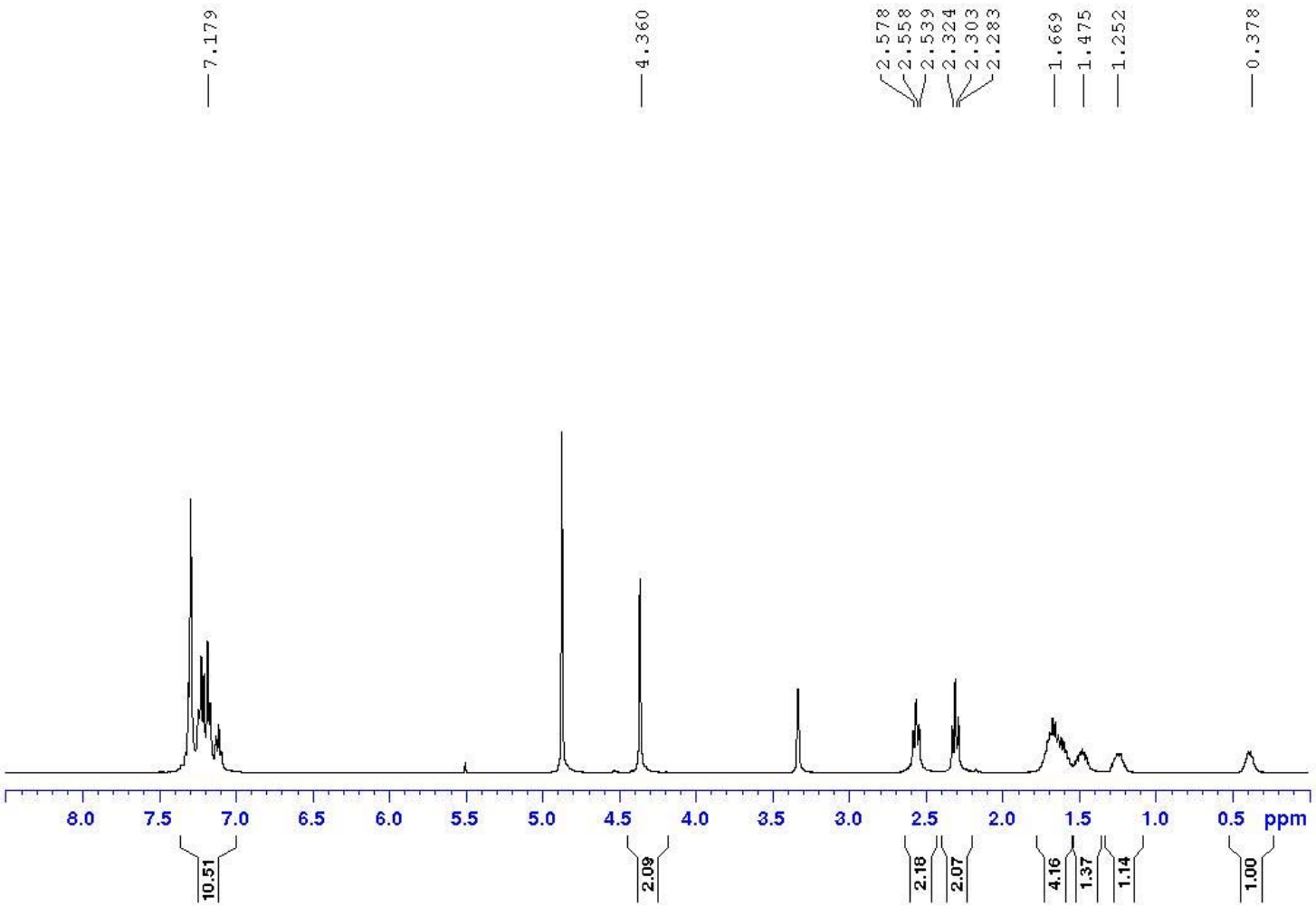


$[\alpha]_D^{20}$	–2.9° (*c* 1.0, MeOH)
m.p.	57.5–58.5 ºC
^{19}F NMR (376 MHz, MeOD)	δ –131.52 (s, BF_3Cs)
^{1}H NMR (400 MHz, MeOD)	δ 7.00–7.40 (10H, m, a,b,b',c,c',n,n',o,o',p), 4.36 (2H, s, l), 2.56 (2H, t, *J* = 7.7 Hz, e), 2.30 (2H, t, *J* = 8.1 Hz, j), 1.55–1.80 (4H, m, f,i), 1.40–1.55 (1H, m, g), 1.20–1.30 (1H, m, g), 0.30–0.50 (1H, m, h)
^{13}C NMR (100 MHz, MeOD)	δ 177.08 (k), 143.66 (d), 138.97 (m), 128.16 (b,b'), 128.14 (o,o'), 127.76 (n,n'), 127.16 (c,c'), 126.74 (p), 124.94 (a), 42.67 (l), 36.67 (e), 36.01 (j), 31.06 (f), 30.79 (g), 27.83 (i)
IR (neat)	3408 (N-H stretch), 3294 2919, 2852, 1640 (C=O stretch), 1521, 1495, 1452 (N-H bend), 1528, 912, 744, 697 cm^{-1}
HRMS (ESI)	$C_{20}H_{24}BF_3NO$ (M-Cs): 362.1903, found 362.1897 *m/z*

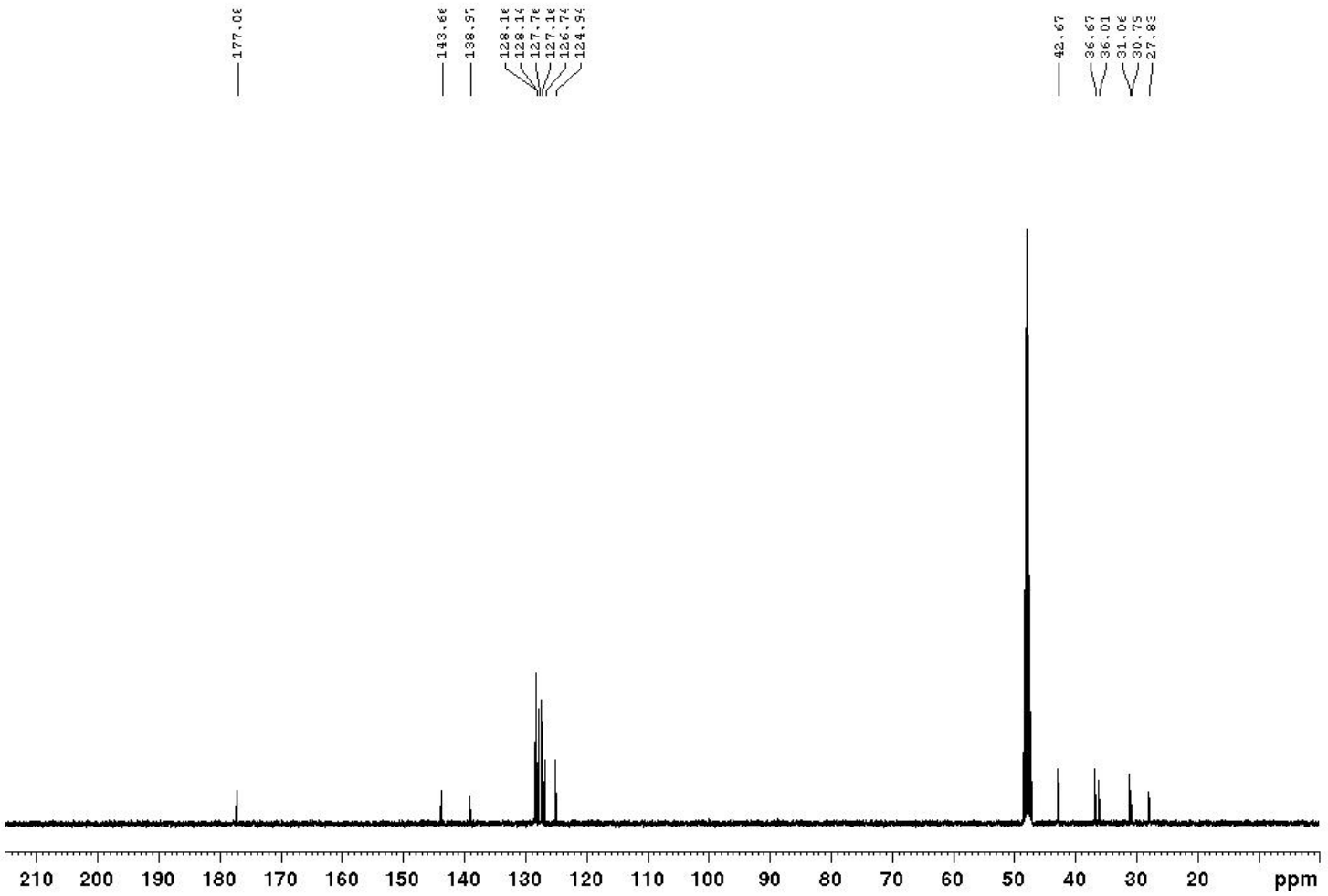
^{19}F NMR of 11d

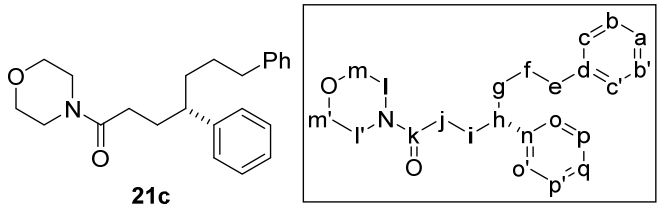


^{1}H NMR of 11d


7.179
4.360
2.578
2.558
2.539
2.324
2.303
2.283
1.669
1.475
1.252
0.378
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
10.51
2.09
2.18
2.07
4.16
1.37
1.14
1.00

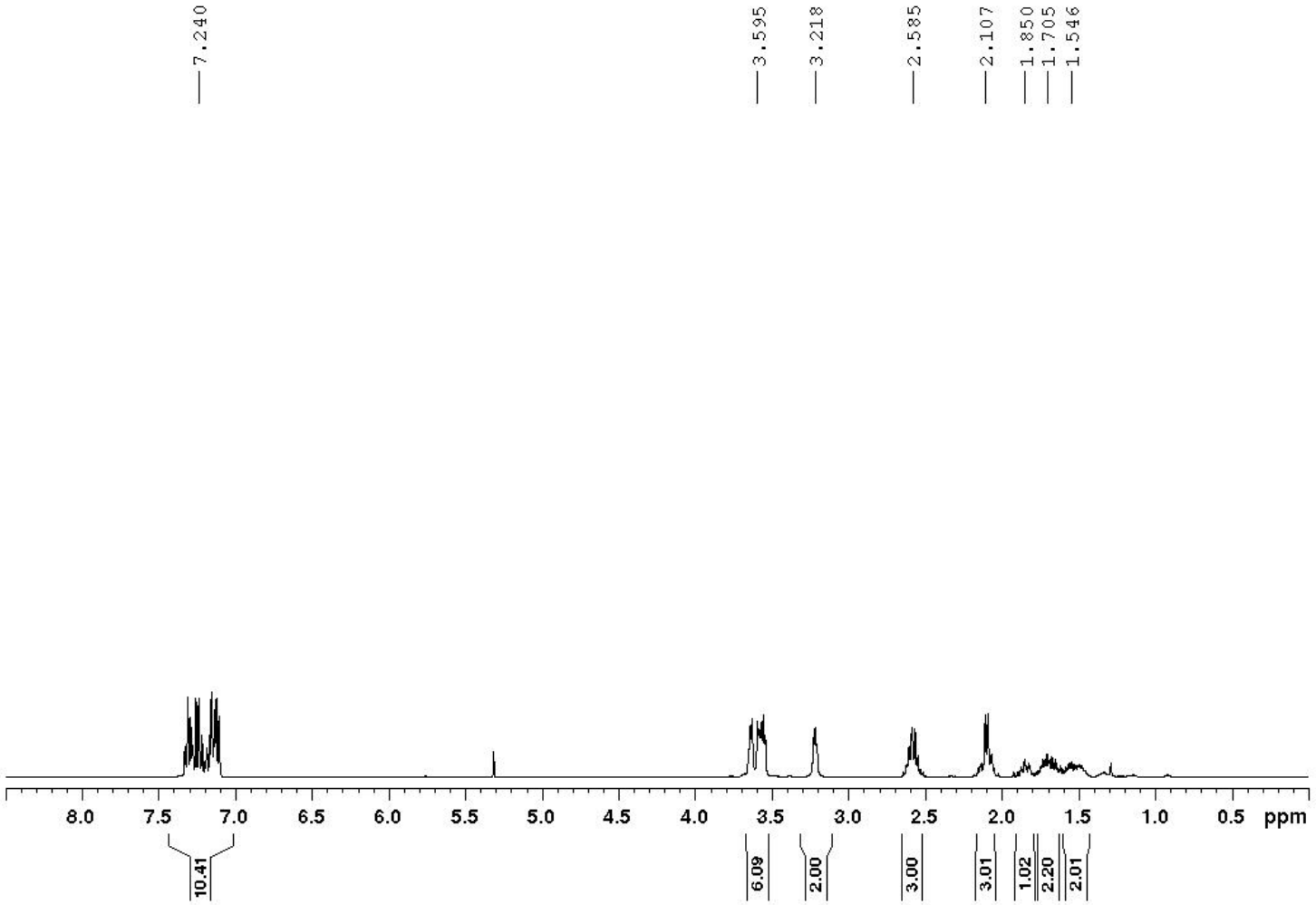
^{13}C NMR of 11d



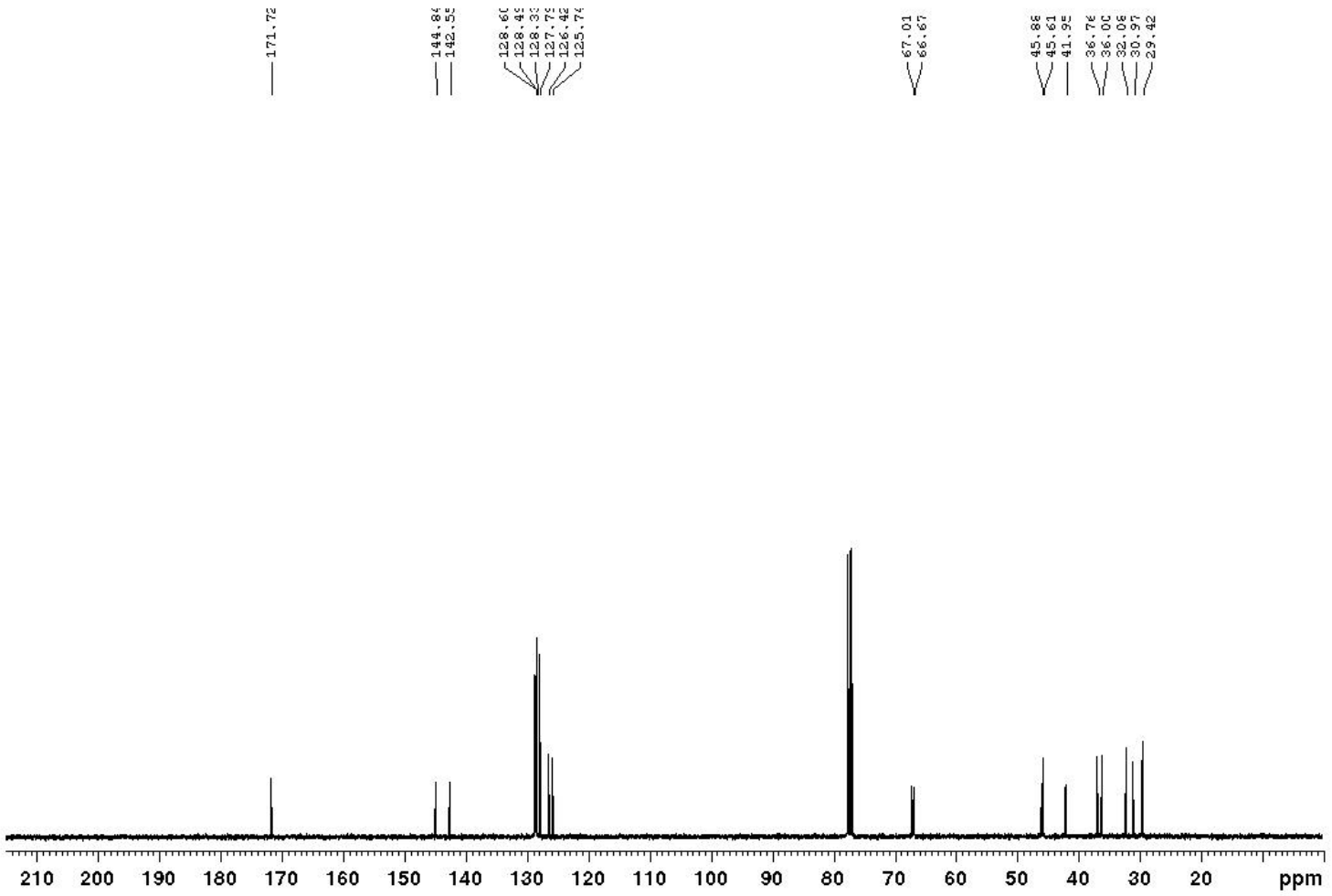


$[\alpha]_D^{20}$	–3.7° (*c* 1.0, $CHCl_3$)
TLC analysis	R_f = 0.4 (80:20 DCM:ethyl acetate)
HPLC analysis	Chiral HPLC analysis (Chiralpak-IC, 80:20 hexanes:isopropanol, flowrate = 1.5 mL/min) showed peaks at 75 minutes (6.5% (*R*)) and 81 minutes (93.5% (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.05–7.35 (10H, m, a,b,b',c,c',o,o',p,p',q), 3.50–3.65 (6H, m, l,l',m,m'), 3.10–3.30 (2H, m, l,l'), 2.50–2.65 (3H, m, e,h), 2.05–2.15 (3H, m, i,j), 1.80–1.90 (1H, m, i), 1.60–1.75 (2H, m, g), 1.45–1.60 (2H, m, f)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 171.72 (k), 144.84 (d), 142.55 (n), 128.60 (b,b'), 128.49 (p,p'), 128.33 (c,c'), 127.79 (o,o'), 126.42 (a), 125.74 (q), 67.01 and 66.67 (m,m'), 45.88 (l,l'), 45.61 (h), 41.95 (l,l'), 36.76 (g), 36.00 (e), 32.08 (i), 30.97 (j), 29.42 (f)
IR (neat)	2919, 2851, 1644 (C=O stretch), 1452, 1426, 1230, 1114, 1029, 747, 699 cm^{-1}
HRMS (ESI)	$C_{23}H_{29}NNaO_2$ (M+Na): 374.2096, found 374.2106 *m/z*

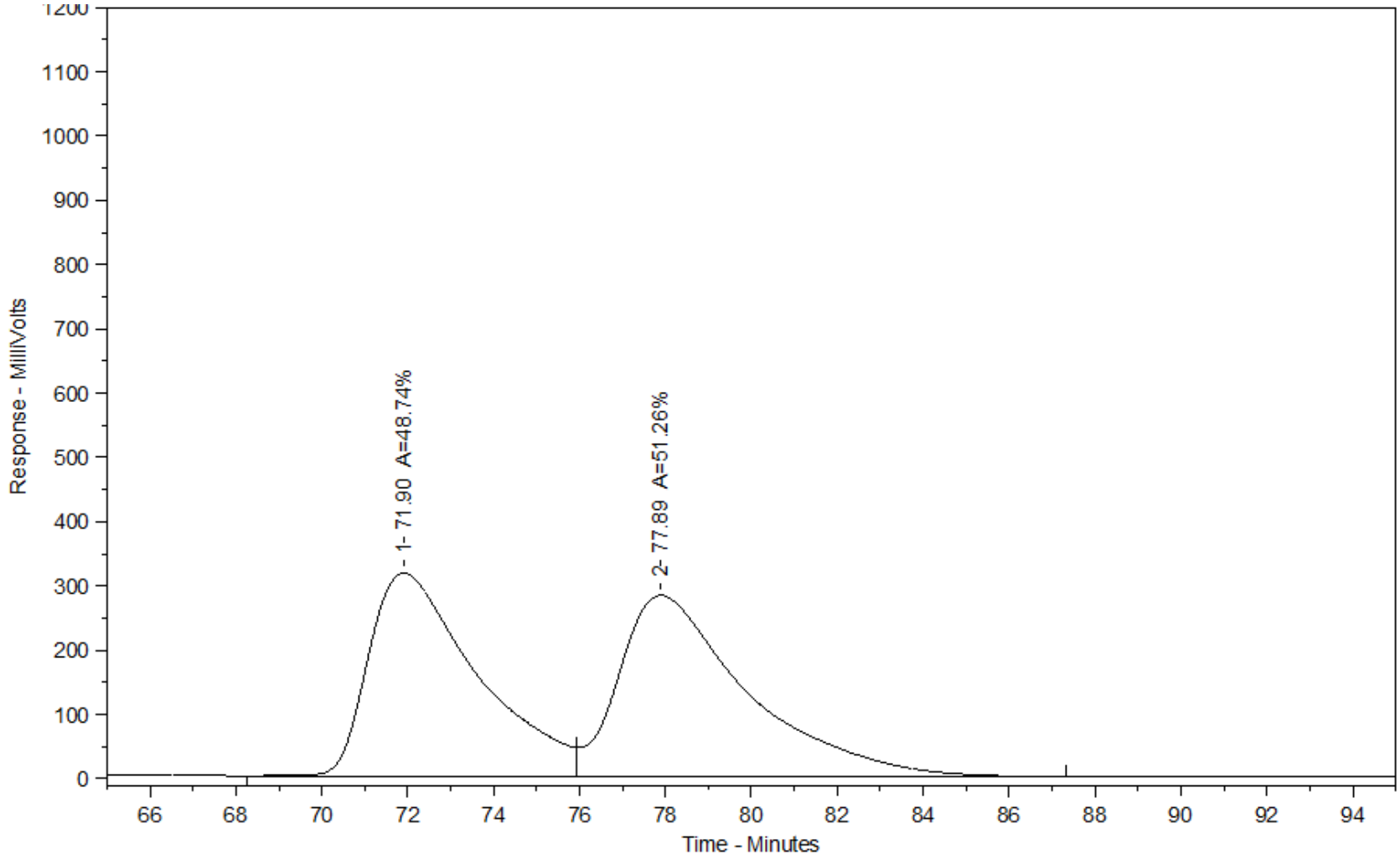
^{1}H NMR of 21c


7.240
3.595
3.218
2.585
2.107
1.850
1.705
1.546
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
10.41
6.09
2.00
3.00
3.01
1.02
2.20
2.01

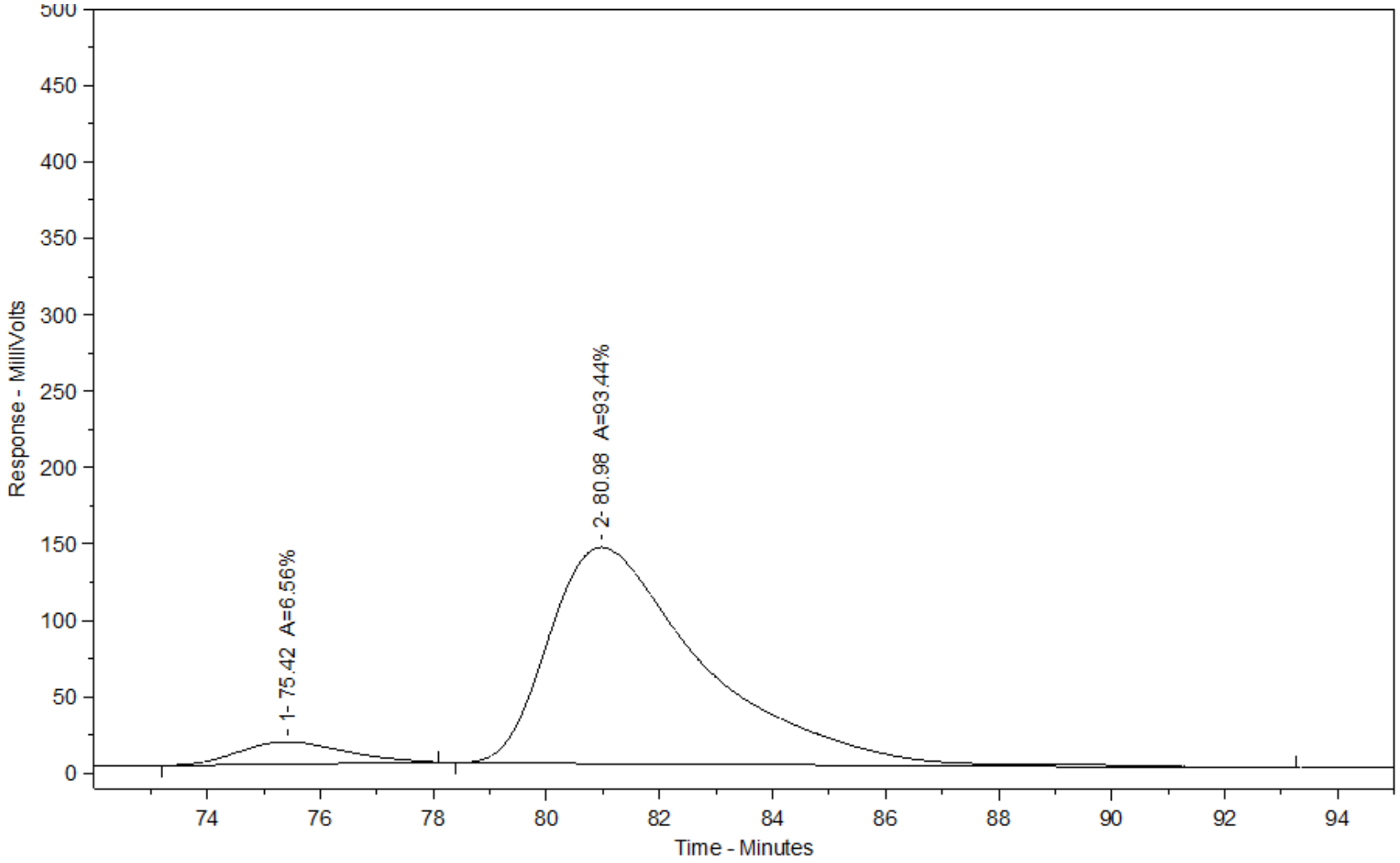
^{13}C NMR of 21c



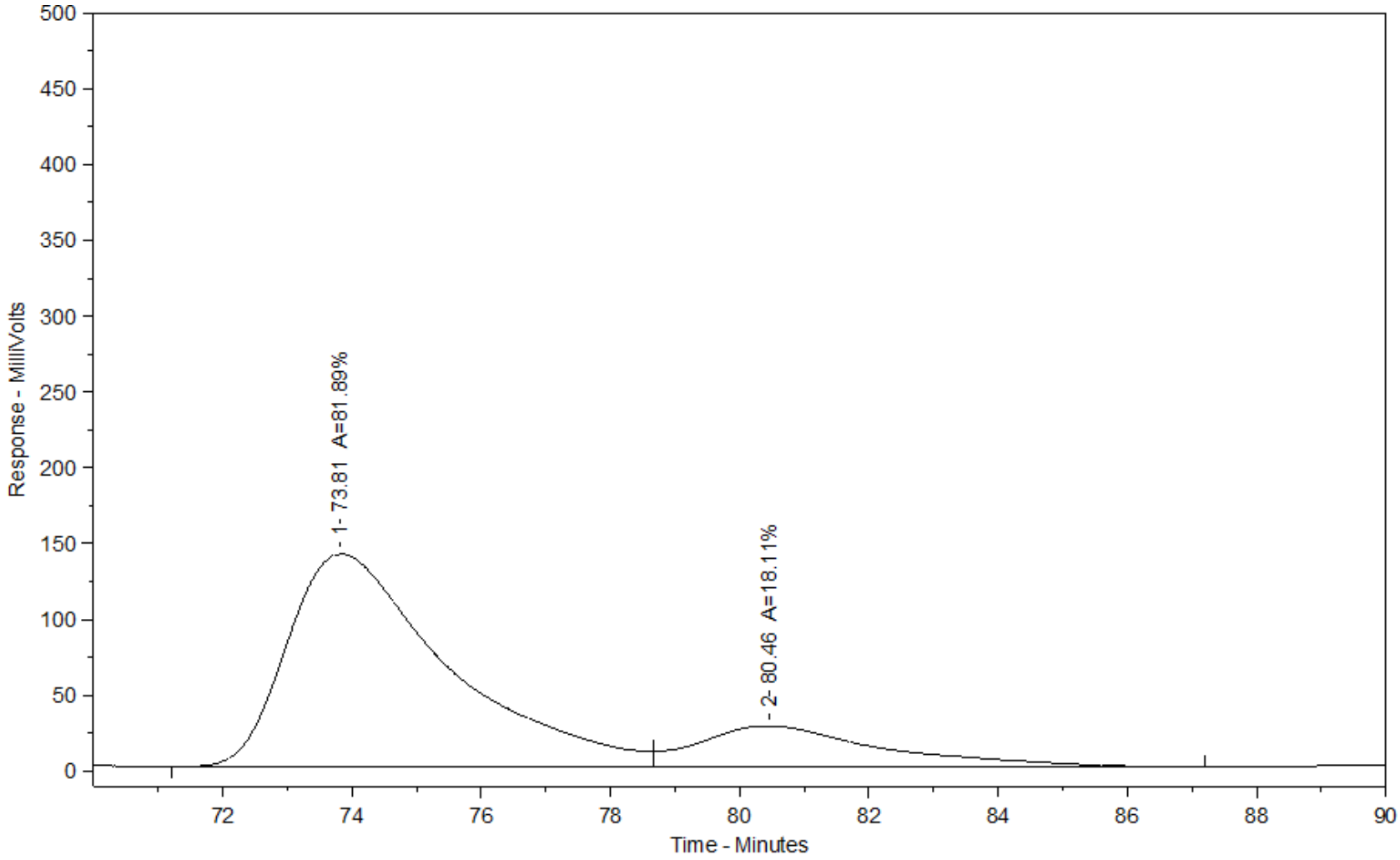
HPLC trace of 21c



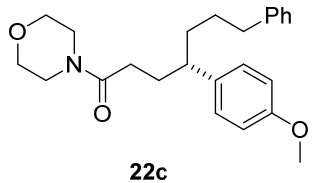
Racemic **21c**



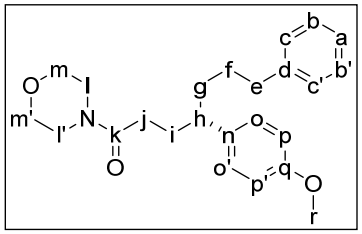
Enantiomeric (*S*)-**21c** (from Suzuki reaction of (*S*)-**11c**)



Enantiomeric (*R*)-**21c** (from alternative synthetic routes)

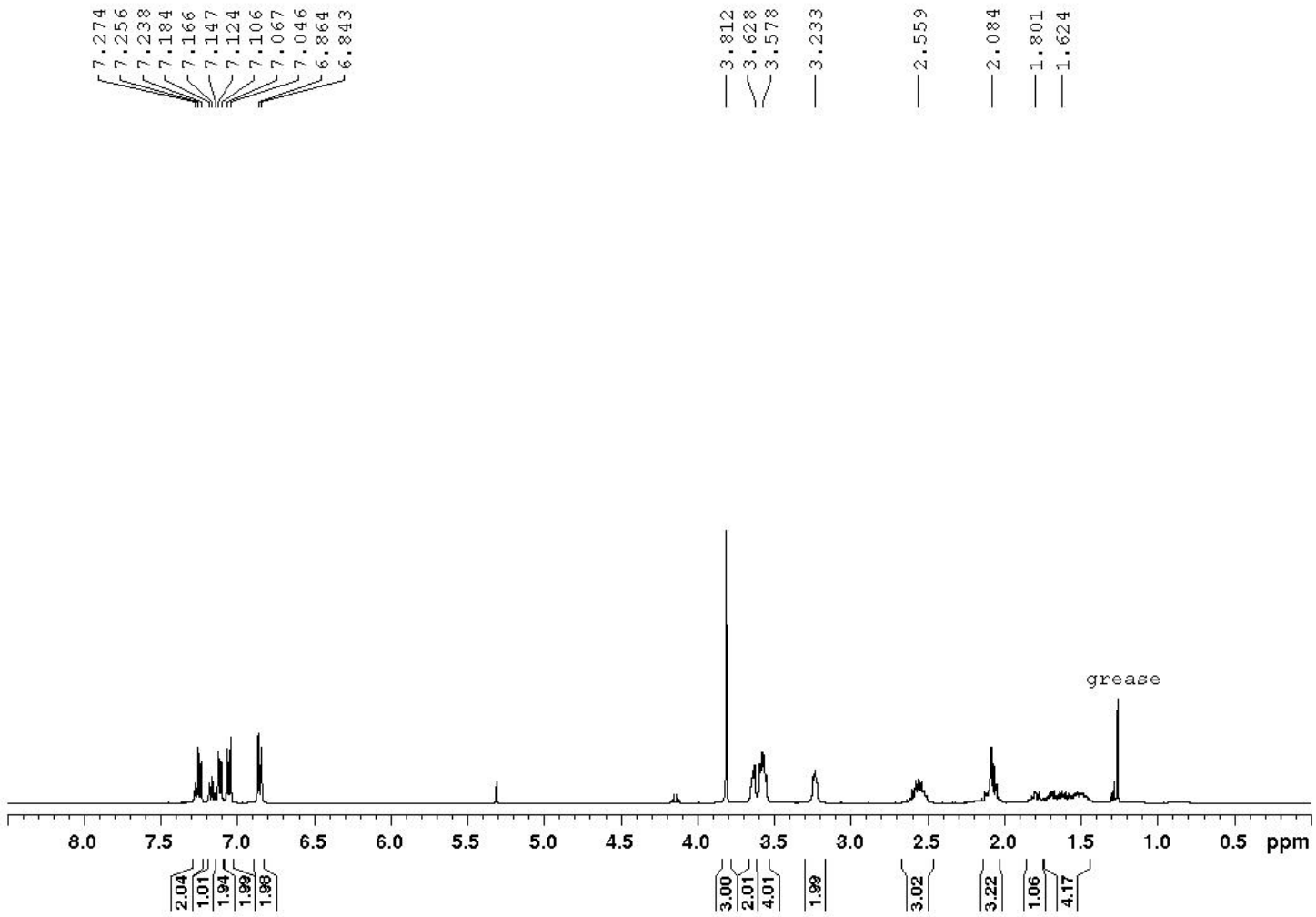


22c

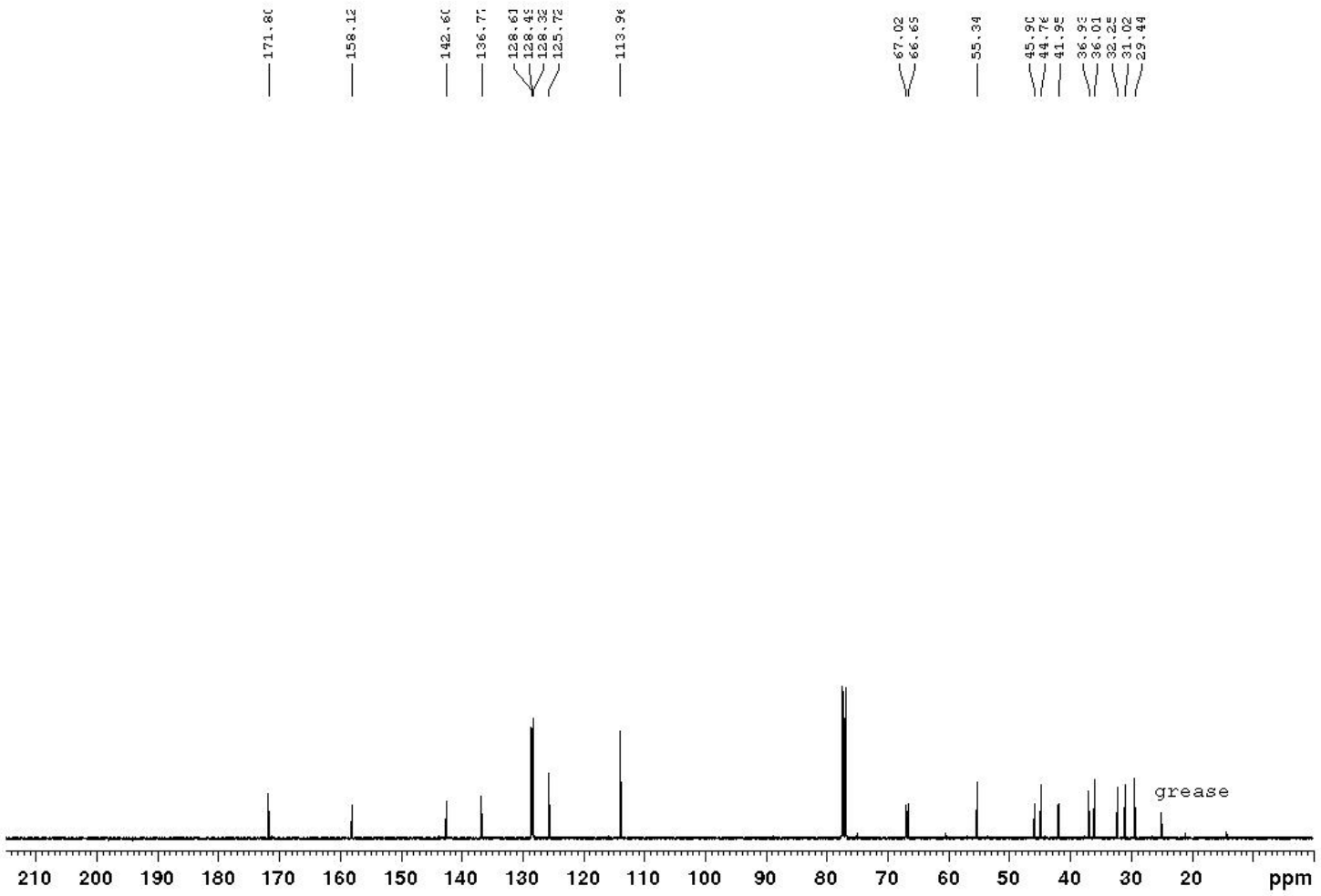


$[\alpha]_D^{20}$	–7.1° (*c* 2.0, $CHCl_3$)
TLC analysis	R_f = 0.4 (80:20 DCM:ethyl acetate)
HPLC analysis	Chiral HPLC analysis ((*S*,*S*)-WHELK-O 1, 50:50 hexanes:isopropanol, flow rate = 1.0 mL/min showed peaks at 25 minutes (6.0% (*R*)) and 28 minutes (94.0% (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.26 (2H, t, *J* = 7.2 Hz, o,o'), 7.17 (1H, t, *J* = 7.3 Hz, a), 7.11 (2H, d, *J* = 7.1 Hz, c,c'), 7.06 (2H, d, *J* = 8.6 Hz, b,b'), 6.85 (2H, d, *J* = 8.6 Hz, p,p'), 3.81 (3H, s, r), 3.60–3.65 (2H, m, m,m'), 3.55–3.60 (4H, m, l,l',m,m'), 3.15–3.30 (2H, m, l,l'), 2.45–2.65 (3H, m, e,h), 2.00–2.15 (3H, m, i,j), 1.75–1.85 (1H, m, i), 1.45–1.75 (4H, m, f,g)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 171.80 (k), 158.12 (q), 142.60 (d), 136.77 (n), 128.61 (b,b'), 128.49 (c,c'), 128.32 (o,o'), 125.72 (a), 113.96 (p,p'), 67.02 and 66.69 (m,m'), 55.34 (r), 45.90 (l,l'), 44.76 (h), 41.95 (l,l'), 36.93 (g), 36.01 (e), 32.25 (i), 31.02 (j), 29.44 (f)
IR (neat)	2920, 2852, 1643 (C=O stretch), 1510, 1426, 1244, 1113, 1030, 831, 700 cm^{-1}
HRMS (ESI)	$C_{24}H_{31}NNaO_3$ (M+Na): 404.2202, found 404.2213 *m/z*

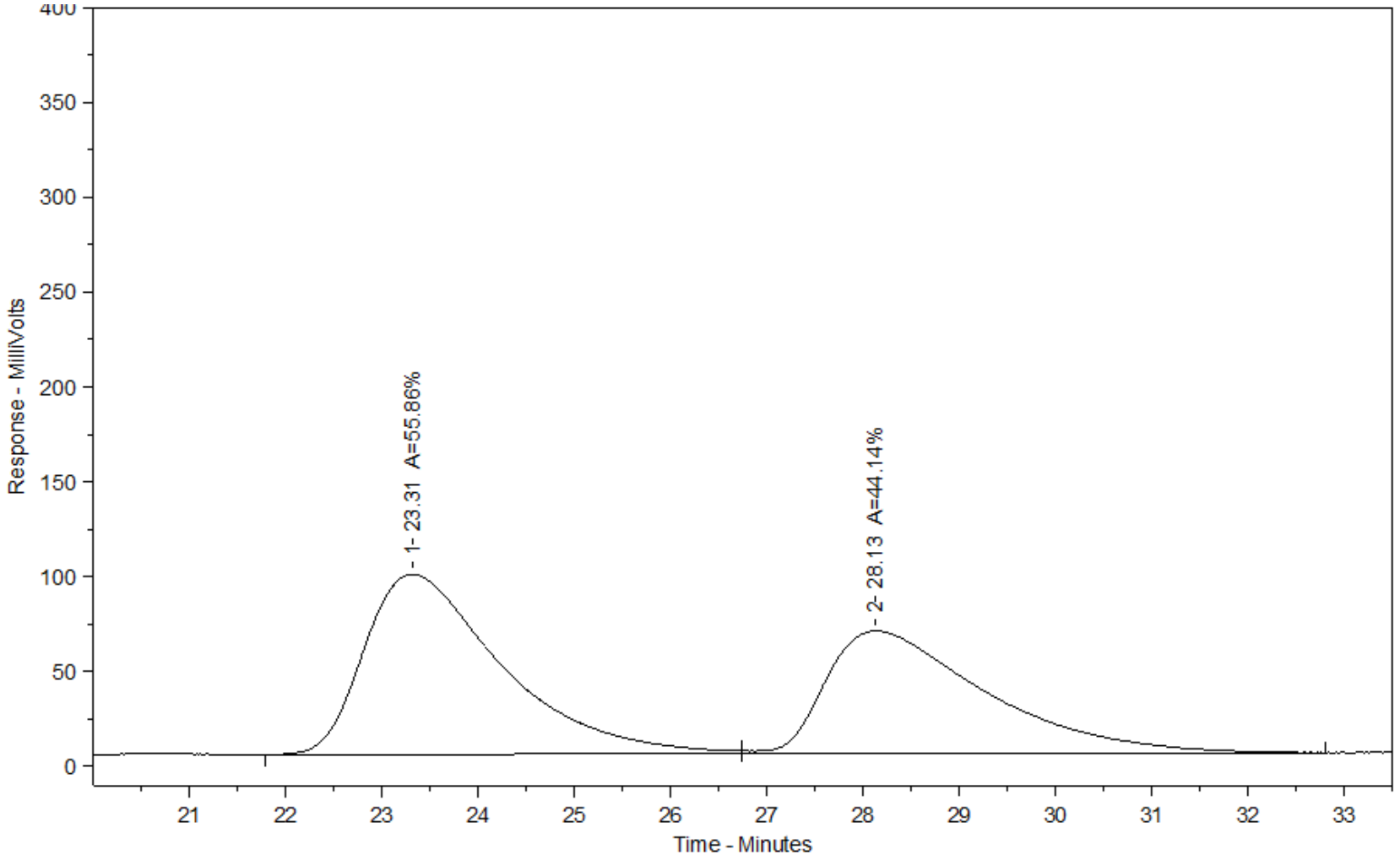
^{1}H NMR of 22c


7.274
7.256
7.238
7.184
7.166
7.147
7.124
7.106
7.067
7.046
6.864
6.843
3.812
3.628
3.578
3.233
2.559
2.084
1.801
1.624
grease
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.04
1.01
1.94
1.99
1.96
3.00
2.01
4.01
1.99
3.02
3.22
1.06
4.17

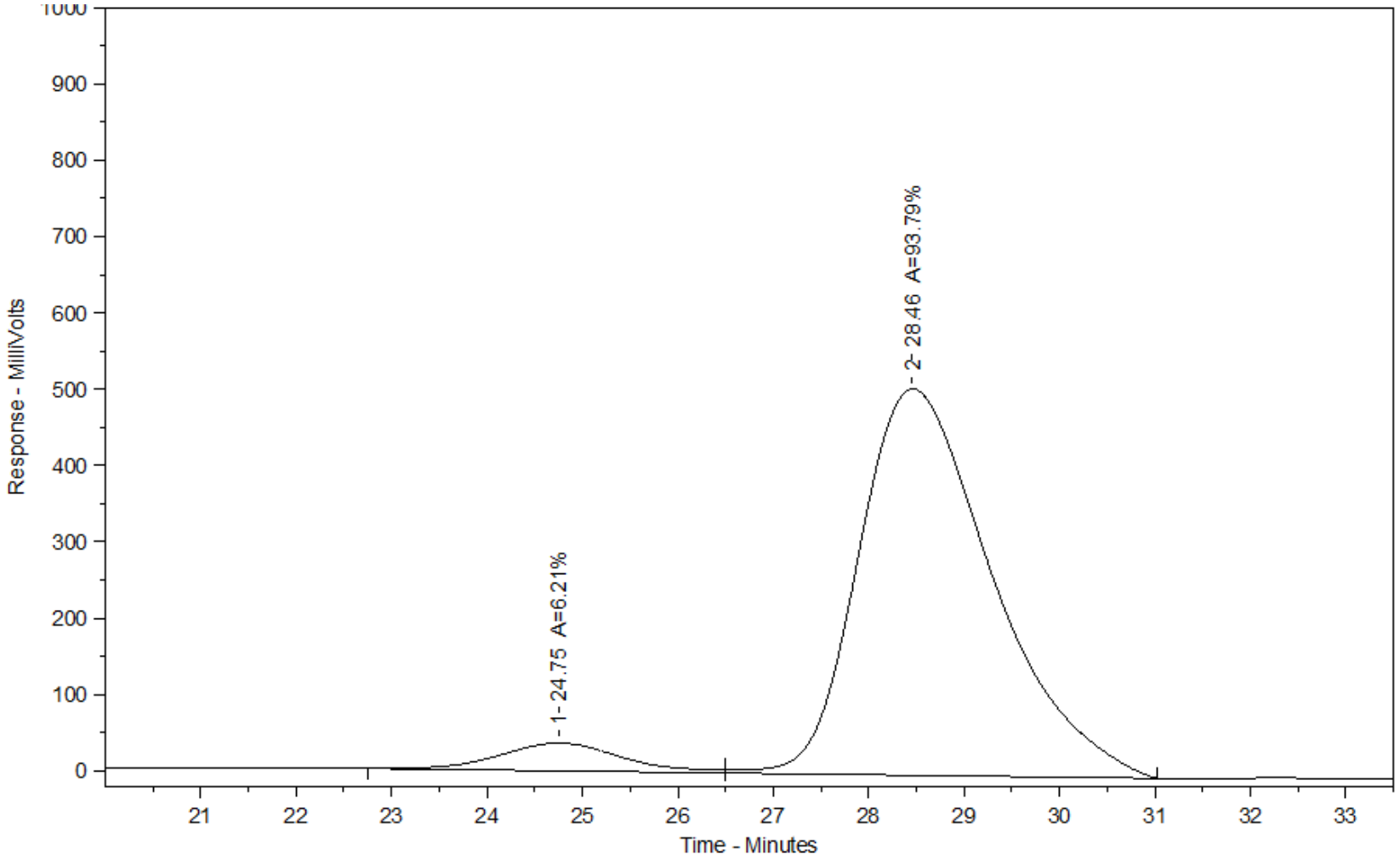
^{13}C NMR of 22c



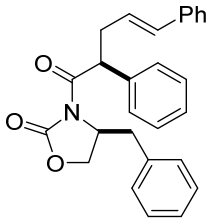
HPLC trace of 22c



Racemic **22c**



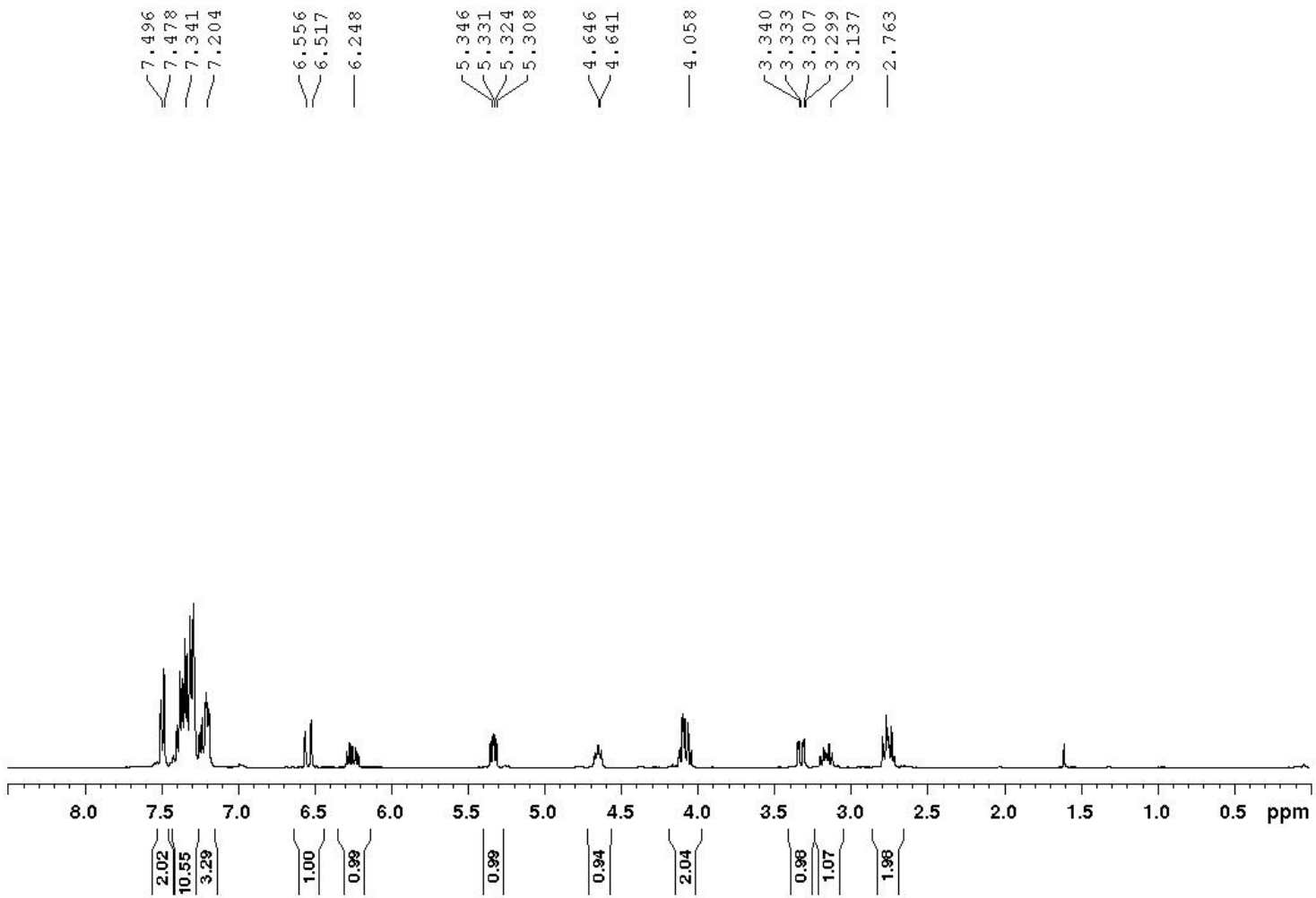
(*S*)-**22c**



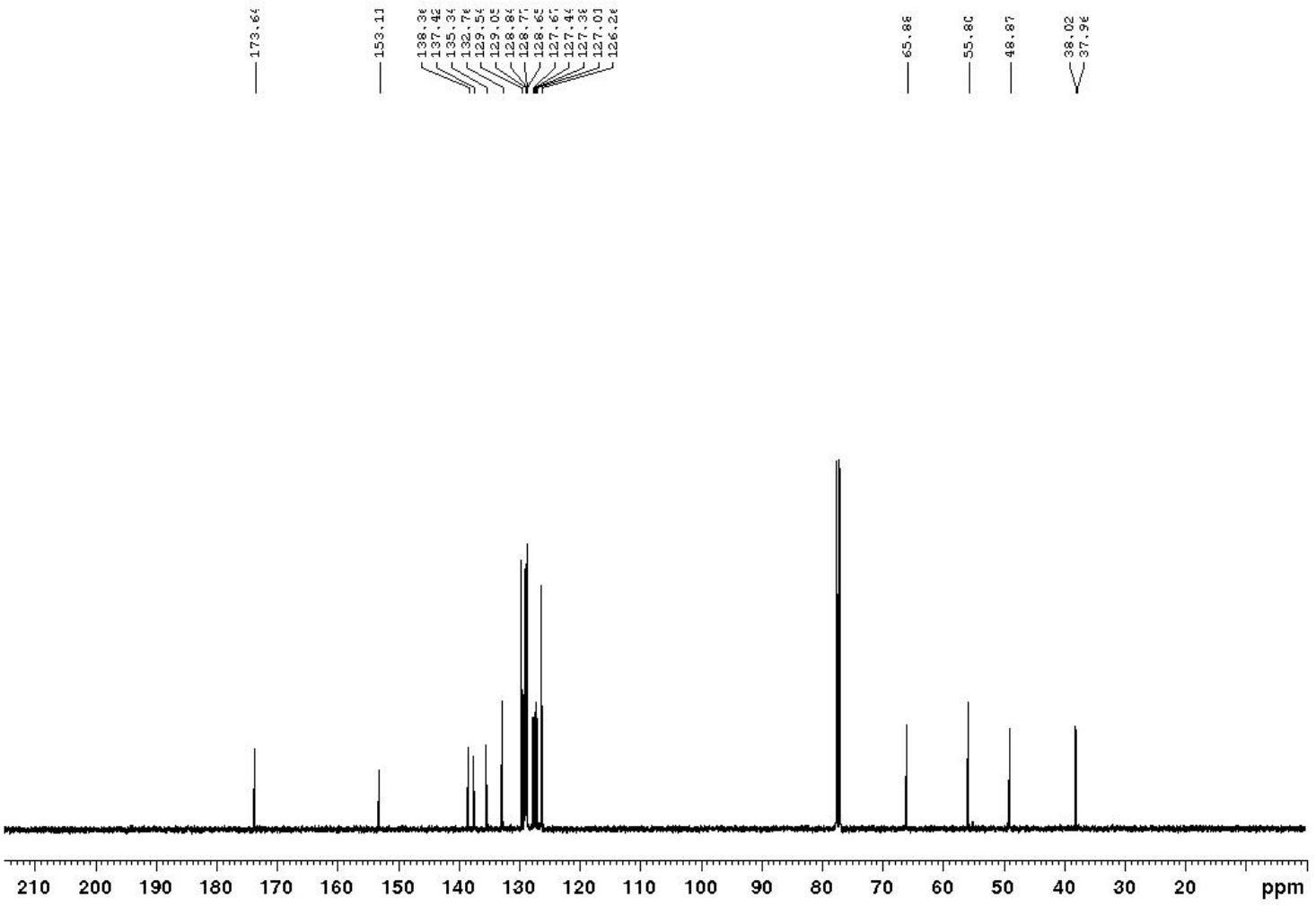
S20

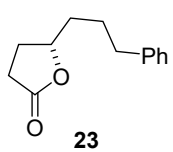
$[\alpha]_D^{20}$	+121° (*c* 1.0, $CHCl_3$)
m.p.	143.5–144.5 °C
TLC analysis	R_f = 0.4 (70:30 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.49 (2H, d, *J* = 7.3 Hz), 7.25–7.45 (10H, m), 7.15–7.25 (3H, m), 6.54 (1H, d, *J* = 15.8 Hz), 6.20–6.30 (1H, m), 5.33 (1H, dd, *J* = 9.0 and 6.2 Hz), 4.60–4.70 (1H, m), 4.00–4.20 (2H, m), 3.32 (1H, dd, *J* = 13.4 and 3.1 Hz), 3.05–3.20 (1H, m), 2.70–2.80 (2H, m)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 173.64, 153.11, 138.36, 137.42, 135.34, 132.76, 129.54, 129.05, 128.84, 128.77, 128.65, 127.67, 127.44, 127.38, 127.01, 126.26, 65.88, 55.80, 48.87, 38.02, 37.96
IR (neat)	3029, 1762 (C=O stretch), 1691 (C=O stretch), 1494, 1392, 1369, 1349, 1243, 1224, 1210, 1185, 1109, 1053, 984, 969, 743, 716, 700, 690 cm^{-1}
HRMS (ESI)	$C_{27}H_{25}NNaO_3$ (M+Na): 434.1732, found 434.1738 *m/z*

^{1}H NMR of S20

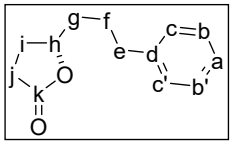

7.496
7.478
7.341
7.204
6.556
6.517
6.248
5.346
5.331
5.324
5.308
4.646
4.641
4.058
3.340
3.333
3.307
3.299
3.137
2.763
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.02
10.55
3.29
1.00
0.99
0.99
0.94
2.04
0.98
1.07
1.98

^{13}C NMR of S20



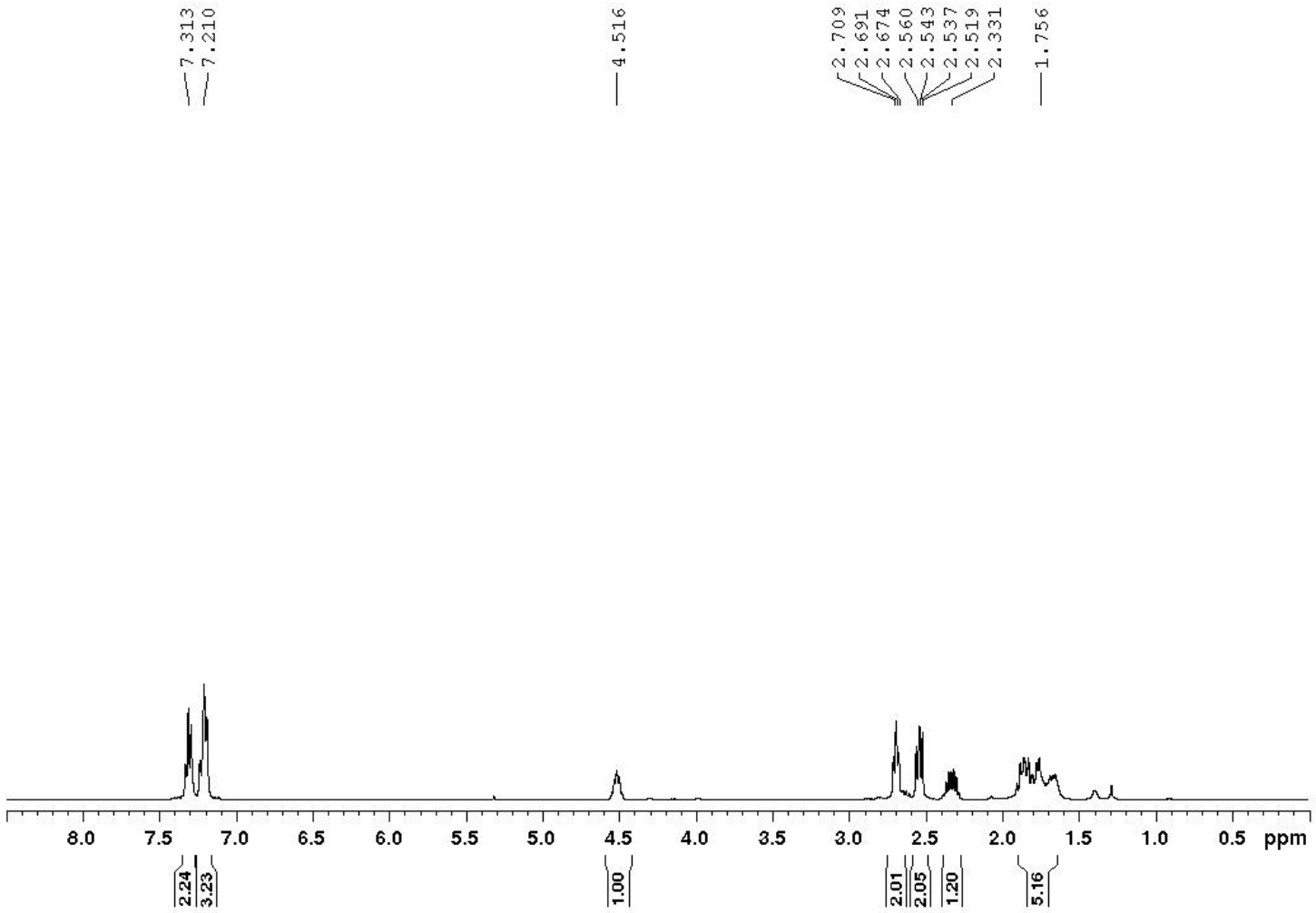


23

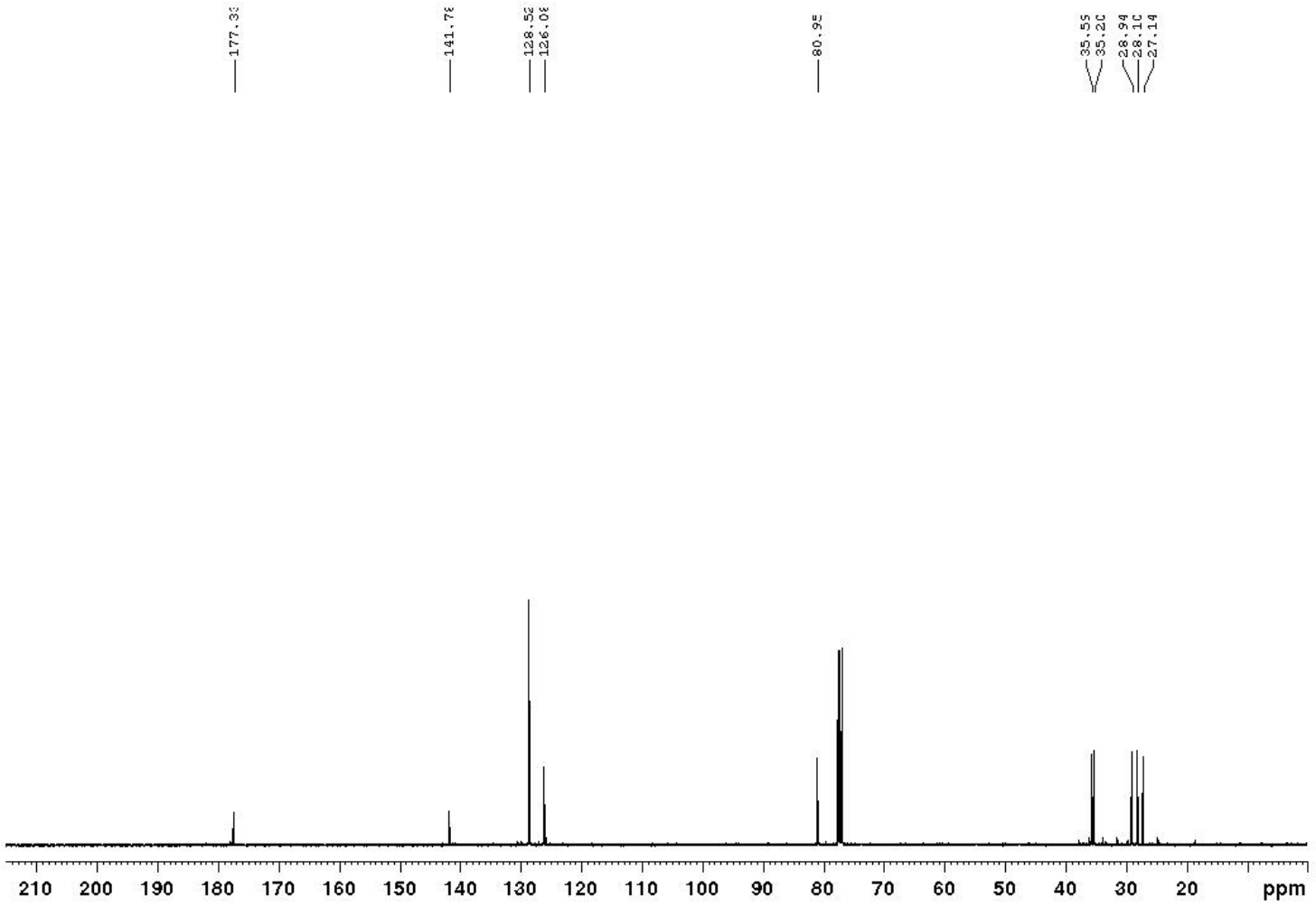


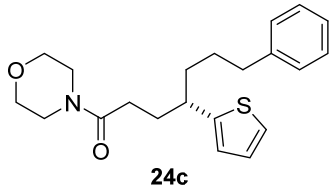
$[\alpha]_D^{20}$	–22.1° (*c* 1.04, $CHCl_3$)
TLC analysis	R_f 0.5 (75:25 hexanes:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.35 (2H, b,b'), 7.15–7.25 (2H, a,c,c'), 4.45–4.60 (1H, m, h), 2.69 (2H, t, *J* = 6.9 Hz, e), 2.54 (2H, dd, *J* = 9.4 and 7.0 Hz, j), 2.25–2.40 (1H, m, i), 1.65–1.90 (5H, m, f,g,i)
^{13}C NMR (100 MHz, $CDCl_3$)	) δ 177.33 (k), 141.78 (d), 128.52 (b,b',c,c'), 126.08 (a), 80.95 (h), 35.59 (e), 35.20 (g), 28.94 (j), 28.10 (i), 27.14 (f)

^{1}H NMR of 23

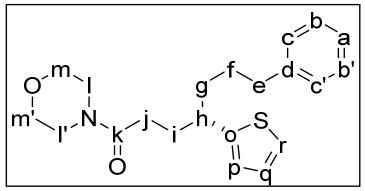

7.313
7.210
4.516
2.709
2.691
2.674
2.560
2.543
2.537
2.519
2.331
1.756
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.24
3.23
1.00
2.01
2.05
1.20
5.16

^{13}C NMR of 23


177.3
141.7
128.5
126.0
80.9
35.5
35.2
28.9
28.1
27.1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

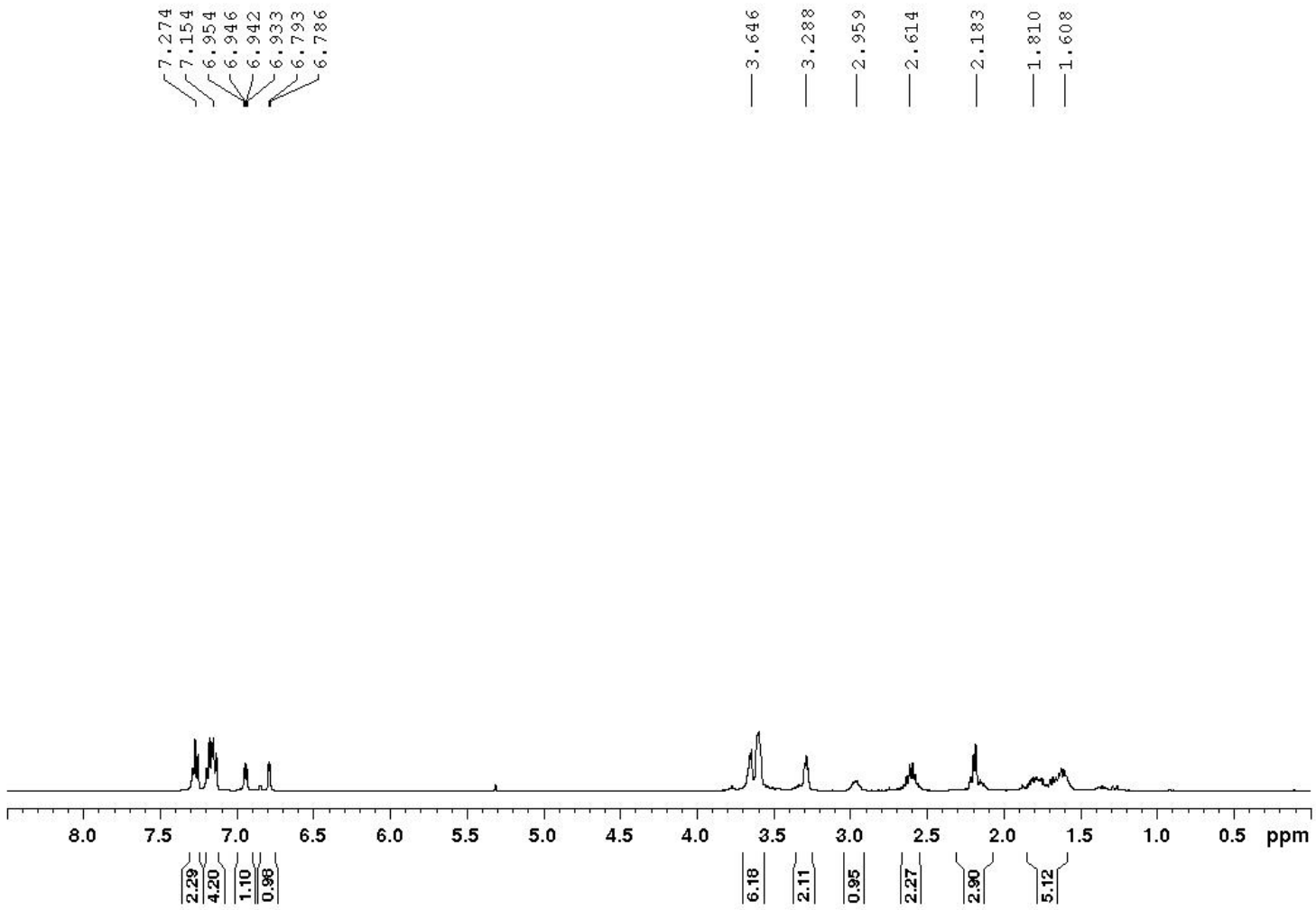


24c

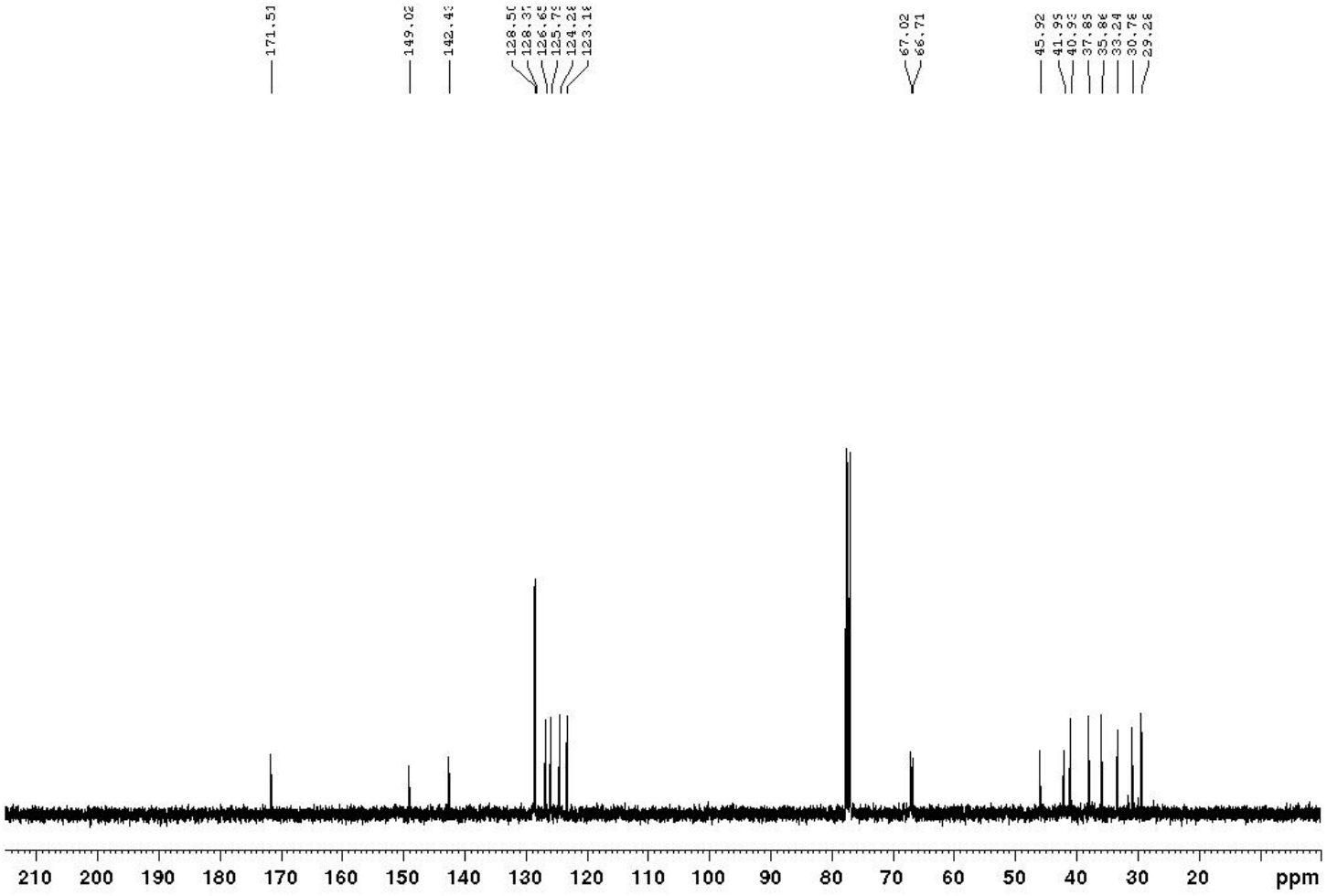


$[\alpha]_D^{20}$	–9.1° (*c* 2.0, $CHCl_3$)
TLC analysis	R_f = 0.4 (80:20 DCM:ethyl acetate)
HPLC analysis	Chiral HPLC analysis (Chiralcel-OJ-H, 100% isopropanol, flow rate = 1.0 mL/min) showed peaks at 12 minutes (5.5% (*R*)) and 18 minutes (94.5% (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.30 (2H, m, c,c'), 7.10–7.20 (4H, m, a,b,b',r), 6.94 (1H, dd, *J* = 4.9 and 3.5 Hz, q), 6.79 (1H, d, *J* = 3.0, p), 3.55–3.70 (6H, m, l,l',m,m'), 3.25–3.35 (2H, m, l,l'), 2.90–3.00 (1H, m, h), 2.55–2.65 (2H, m, e), 2.10–2.25 (3H, m, i,j), 1.55–1.85 (5H, m, f,g,i)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 171.51 (k), 149.02 (o), 142.43 (d), 128.50 (b,b'), 128.37 (c,c'), 126.65 (q), 125.79 (a), 124.28 (p), 123.18 (r), 67.02 and 66.71 (m,m'), 45.92 and 41.99 (l,l'), 40.93 (h), 37.89 (g), 35.86 (e), 33.24 (i), 30.78 (j), 29.28 (f)
IR (neat)	2920, 2853, 1642 (C=O stretch), 1452, 1429, 1229, 1113, 697 cm^{-1}
HRMS (ESI)	$C_{21}H_{27}NNaO_2S$ (M+Na): 380.1660, found 380.1678 *m/z*

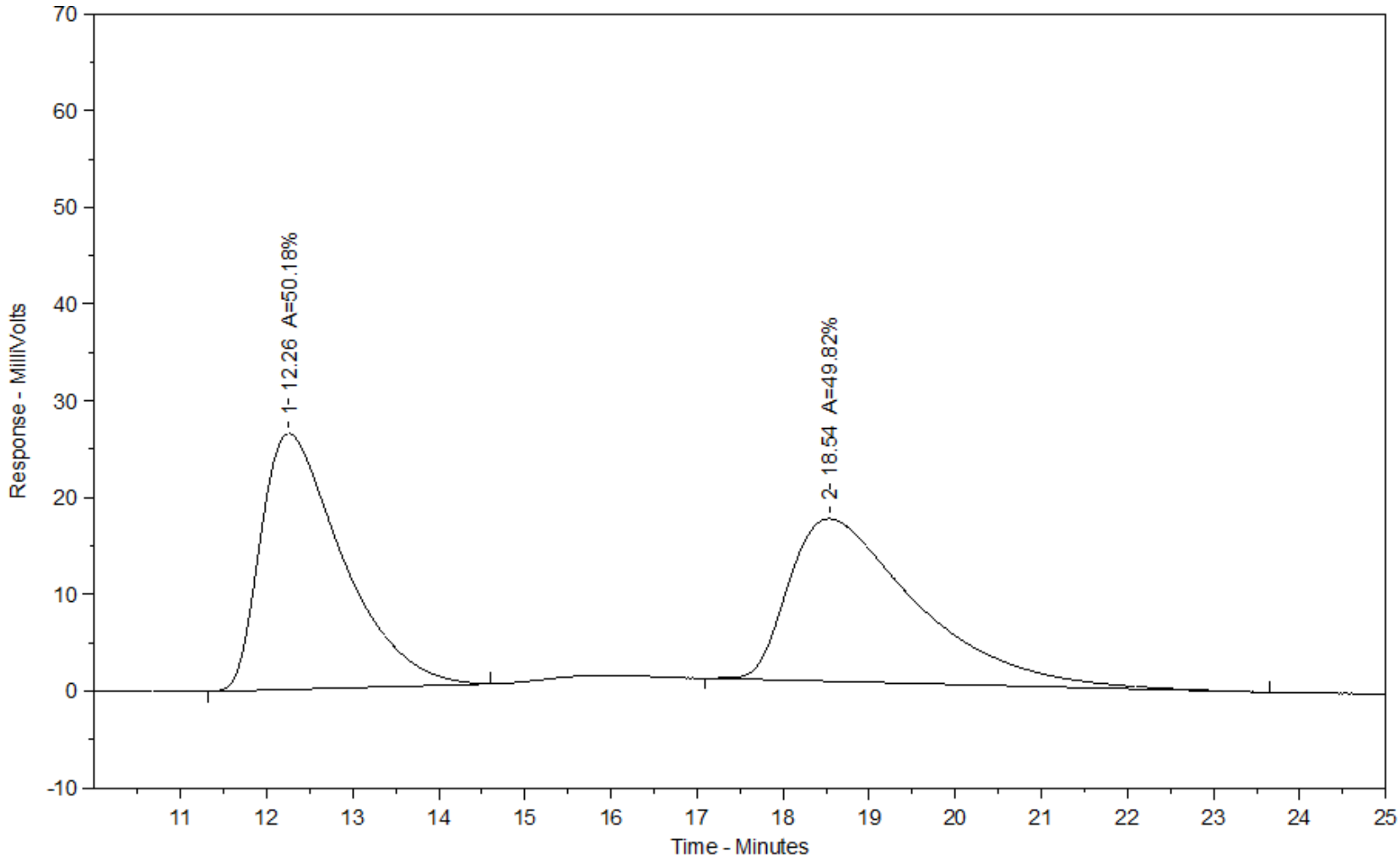
^{1}H NMR of 24c


7.274
7.154
6.954
6.946
6.942
6.933
6.793
6.786
3.646
3.288
2.959
2.614
2.183
1.810
1.608
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
2.29
4.20
1.10
0.98
6.18
2.11
0.95
2.27
2.90
5.12

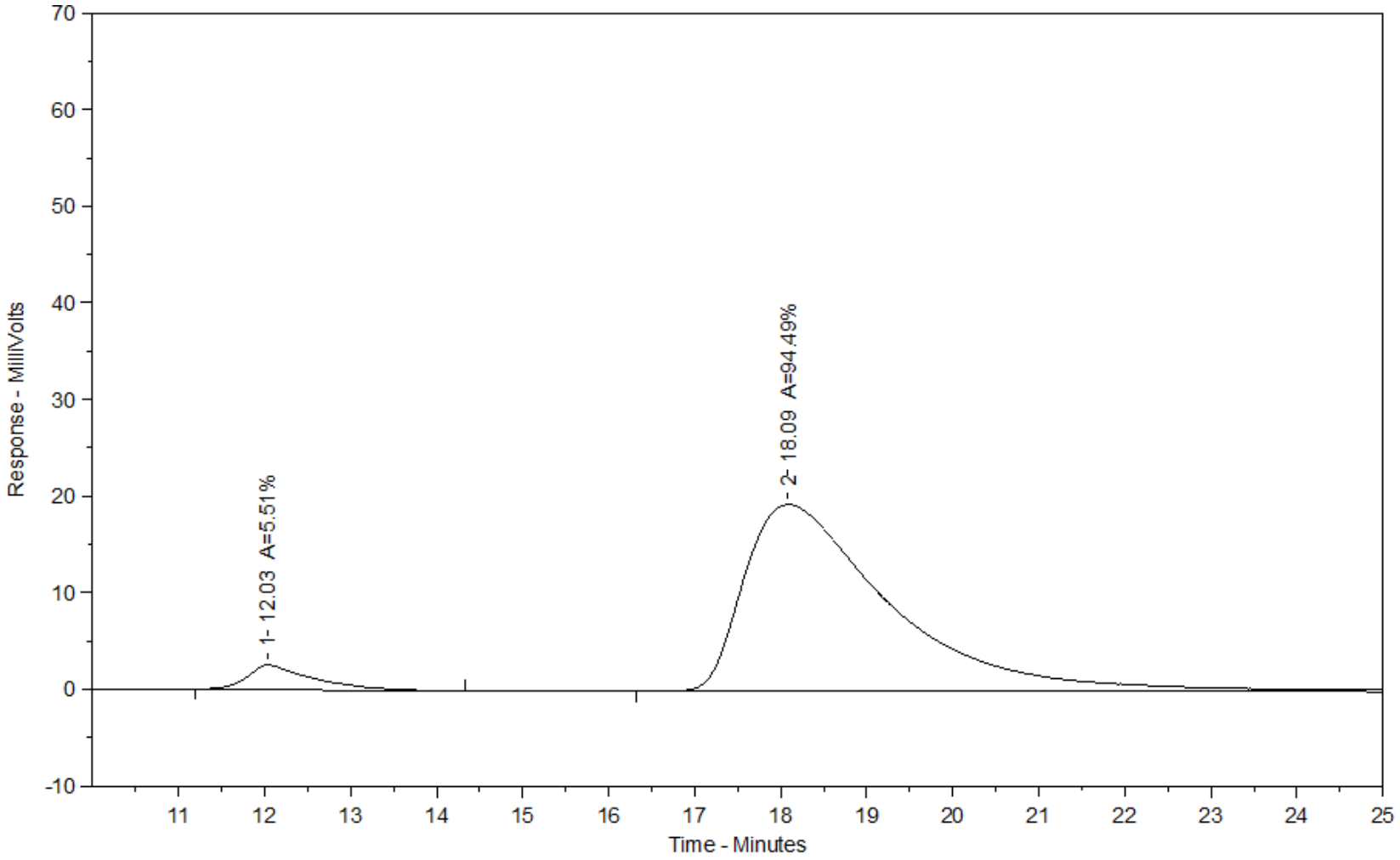
^{13}C NMR of 24c



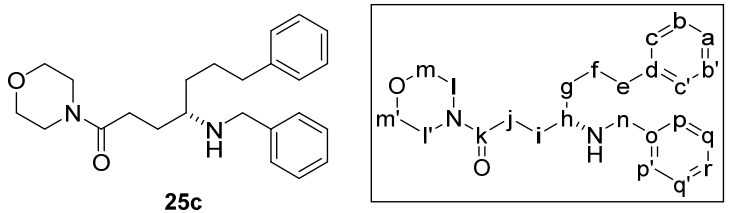
HPLC trace of 24c



Racemic **24c**



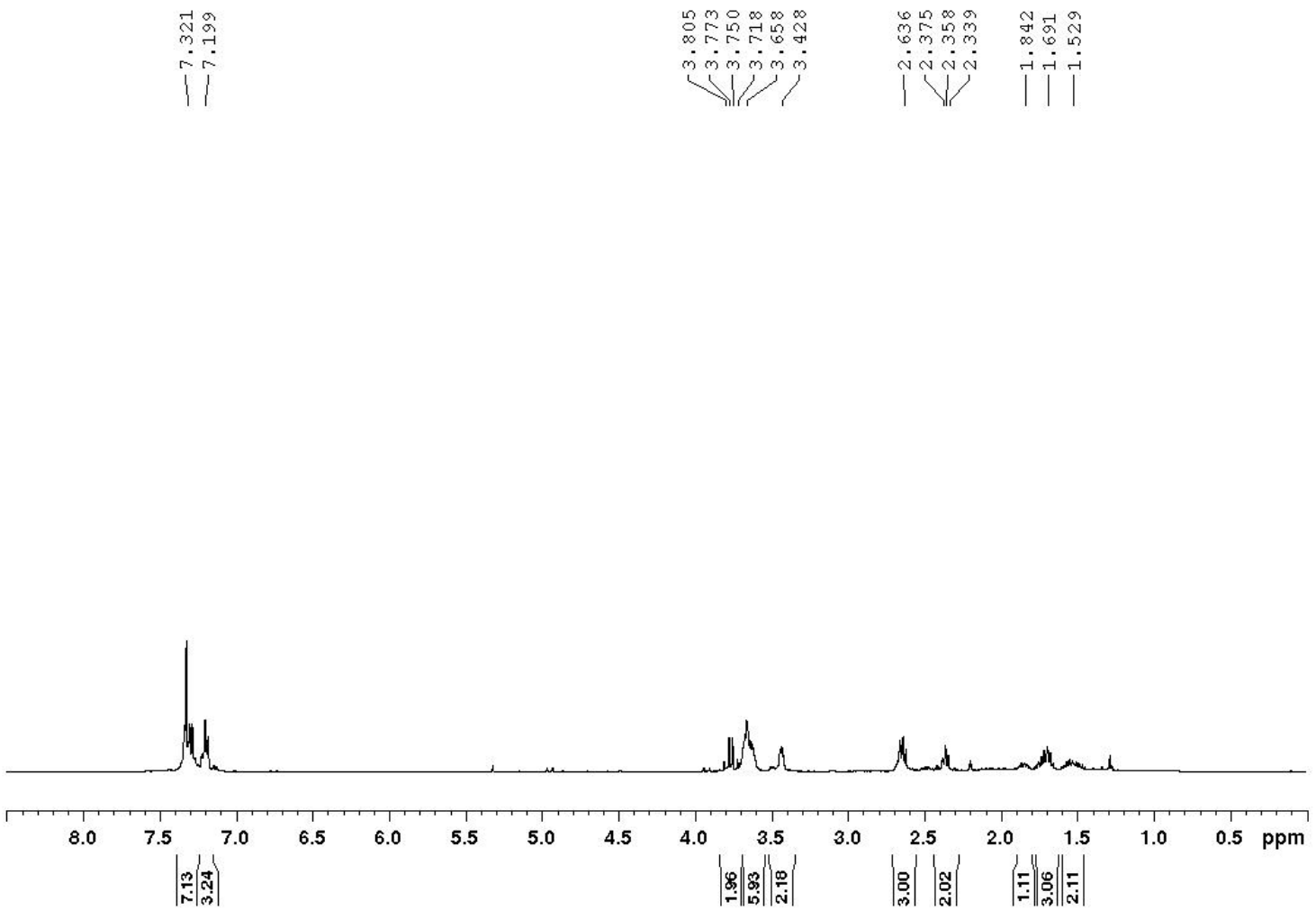
(*S*)-**24c**



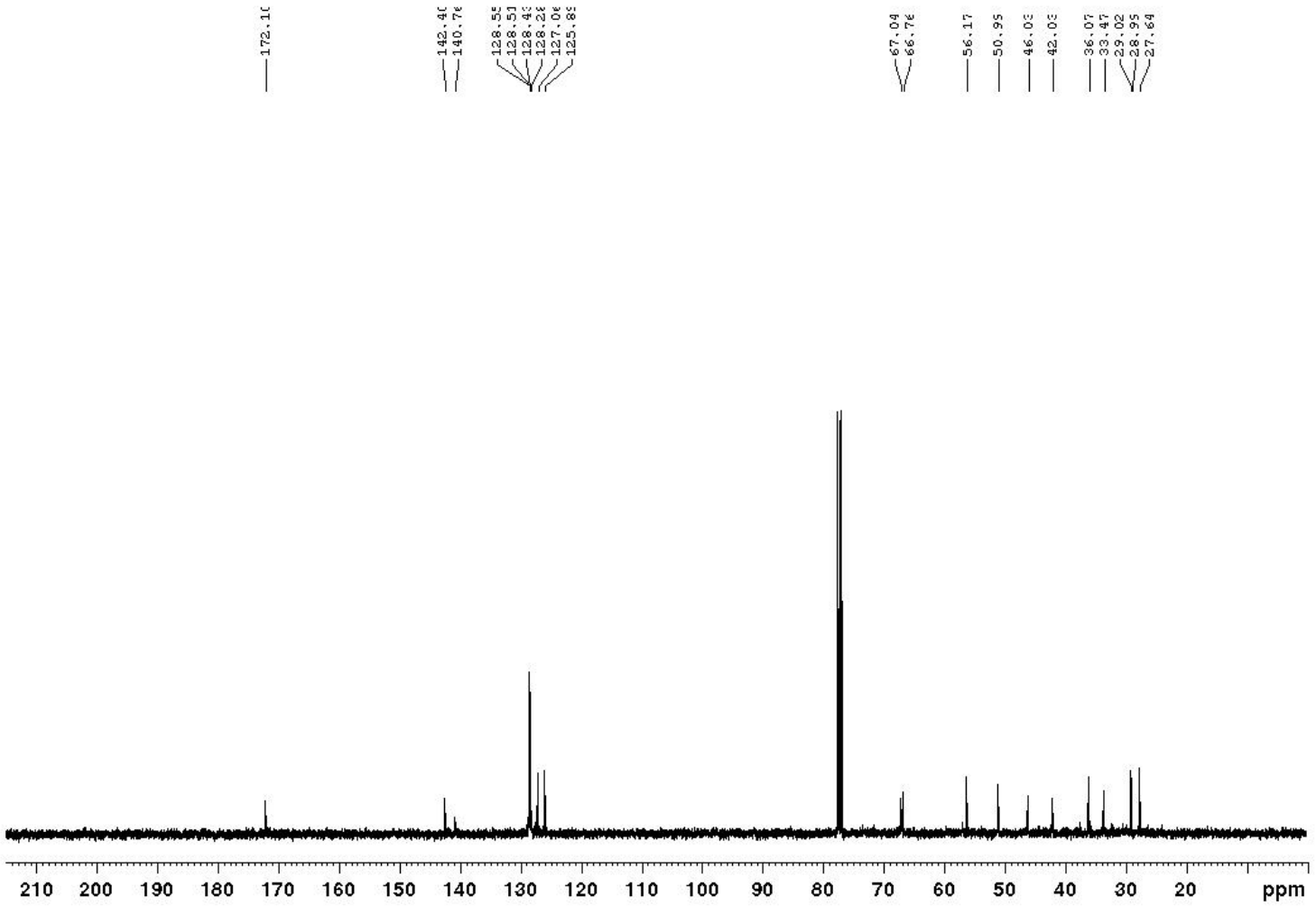
25c

$[\alpha]_D^{20}$	+7.5° (*c* 1.5, $CHCl_3$)
TLC analysis	R_f 0.2 (5:95 methanol:ethyl acetate)
HPLC analysis	Chiral HPLC analysis (Chiralcel-OJ-H, 90:10 hexanes:isopropanol, flow rate = 1.5 mL/min) showed peaks at 18 minutes (94.0% (*S*)) and 20 minutes (6.0% (*R*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.25–7.35 (7H, m, c,c',p,p',q,q',r), 7.15–7.25 (3H, a,b,b'), 3.70–3.80 (2H, m, n), 3.55–3.70 (6H, m, l,l',m,m'), 3.35–3.50 (2H, m, l,l'), 2.60–2.70 (3H, m, e,h), 2.36 (2H, t, *J* = 7.5 Hz, j), 1.80–1.90 (1H, m, i), 1.60–1.80 (1H, m, f,i), 1.45–1.60 (2H, m, g)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.10 (k), 142.40 (d), 140.76 (o), 128.55 (b,b'), 128.51 (q,q'), 128.43 (c,c'), 128.28 (p,p'), 127.06 (r), 125.89 (a), 67.04 and 66.76 (m,m'), 56.17 (h), 50.99 (n), 46.03 and 42.03 (l,l'), 36.07 (e), 33.47 (g), 29.02 (j), 28.99 (i), 27.64 (f)
IR (neat)	2934, 2854, 1640 (C=O stretch), 1452, 1430, 1114, 746, 698 cm^{-1}
HRMS (ESI)	$C_{24}H_{32}N_2NaO_2$ (M+Na): 403.2361, found 403.2363 *m/z*

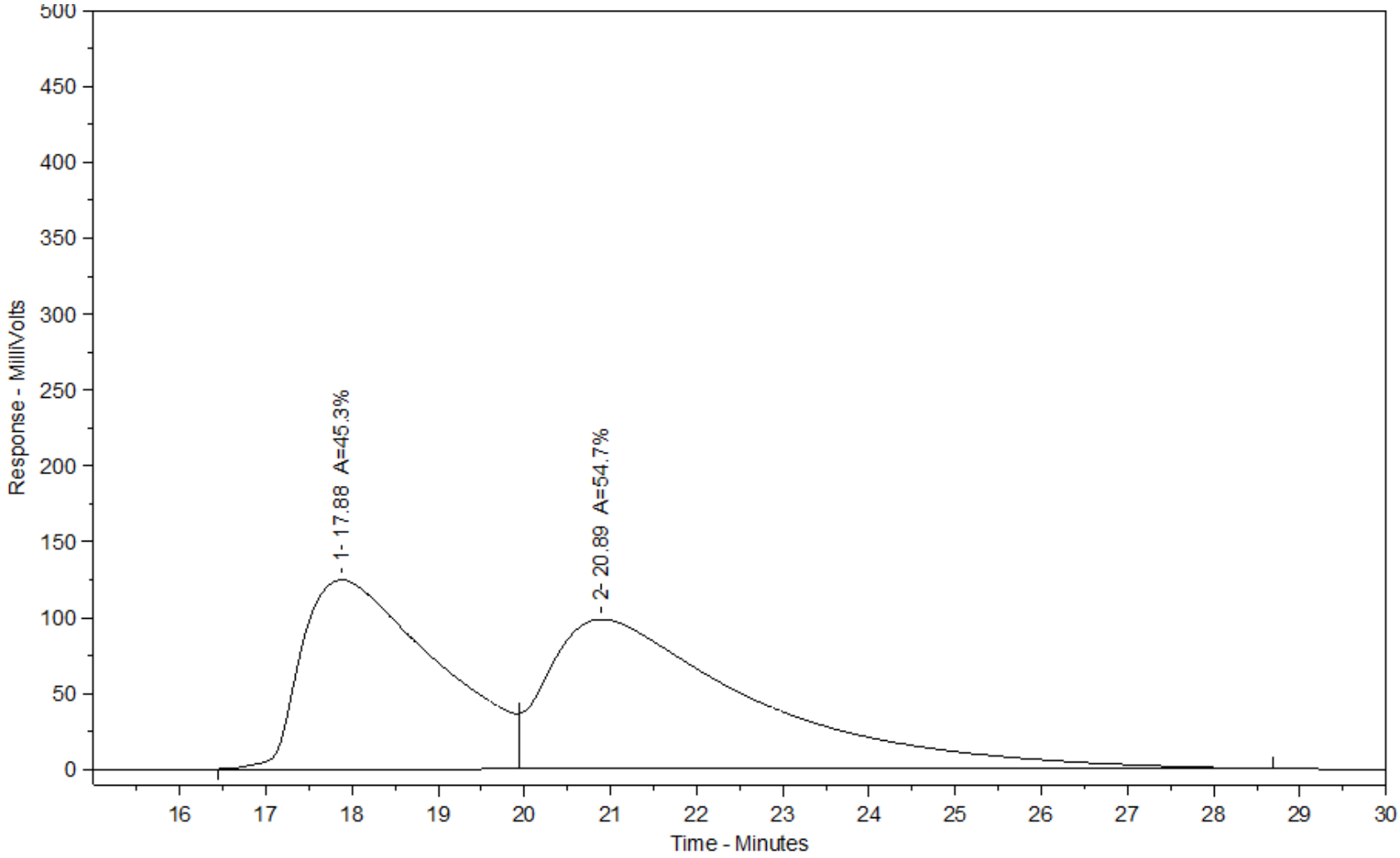
^{1}H NMR of 25c


7.321
7.199
3.805
3.773
3.750
3.718
3.658
3.428
2.636
2.375
2.358
2.339
1.842
1.691
1.529
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
7.13
3.24
1.96
5.93
2.18
3.00
2.02
1.11
3.06
2.11

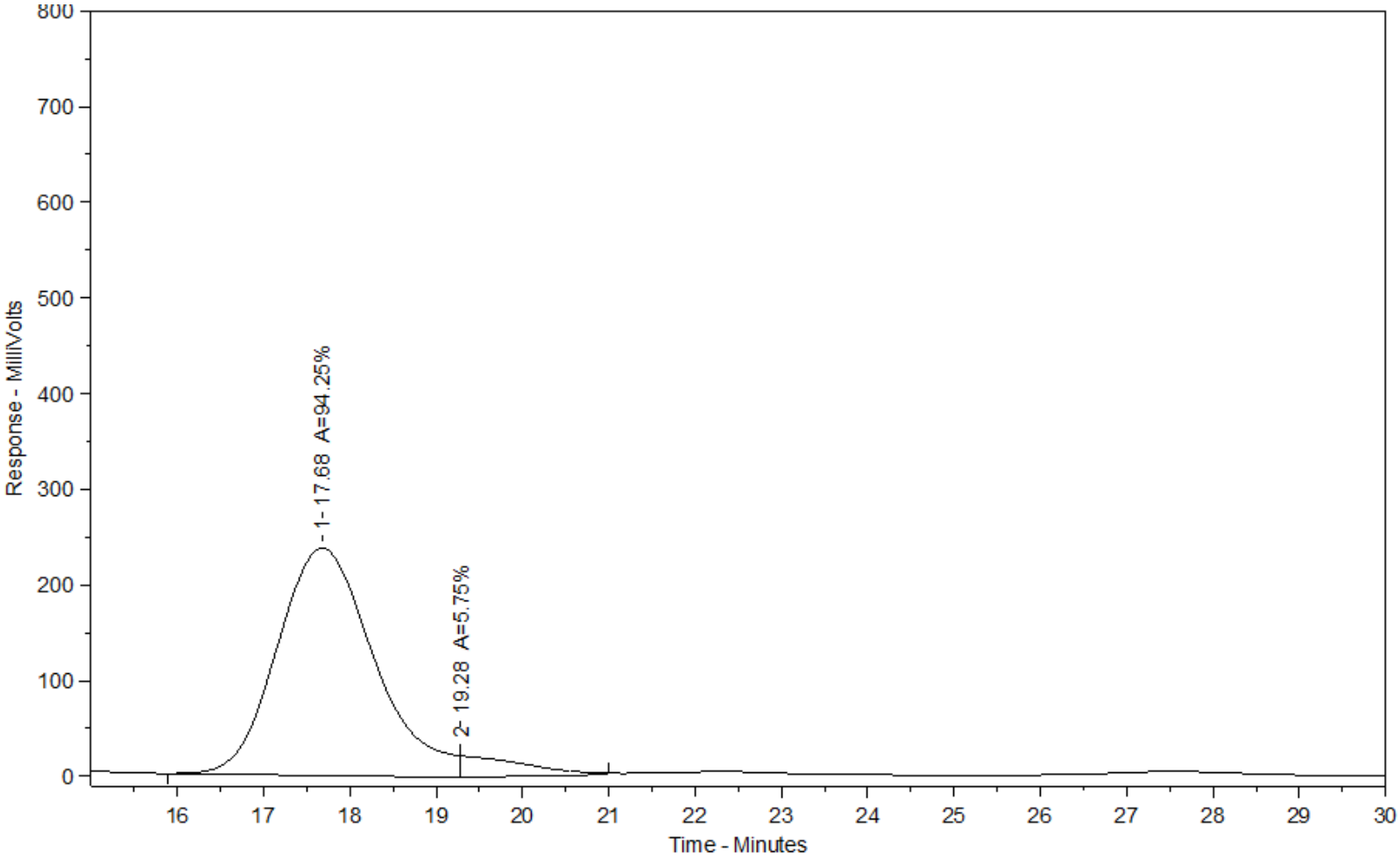
^{13}C NMR of 25c



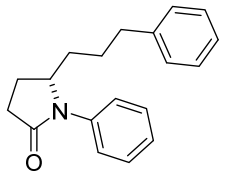
HPLC trace of 25c



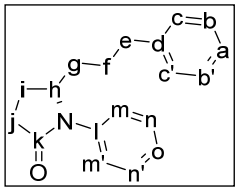
Racemic **25c**


Response - MilliVolts
Time - Minutes
1- 17.68 A=94.25%
2- 19.28 A=5.75%
0
100
200
300
400
500
600
700
800
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30

(*S*)-**25c**

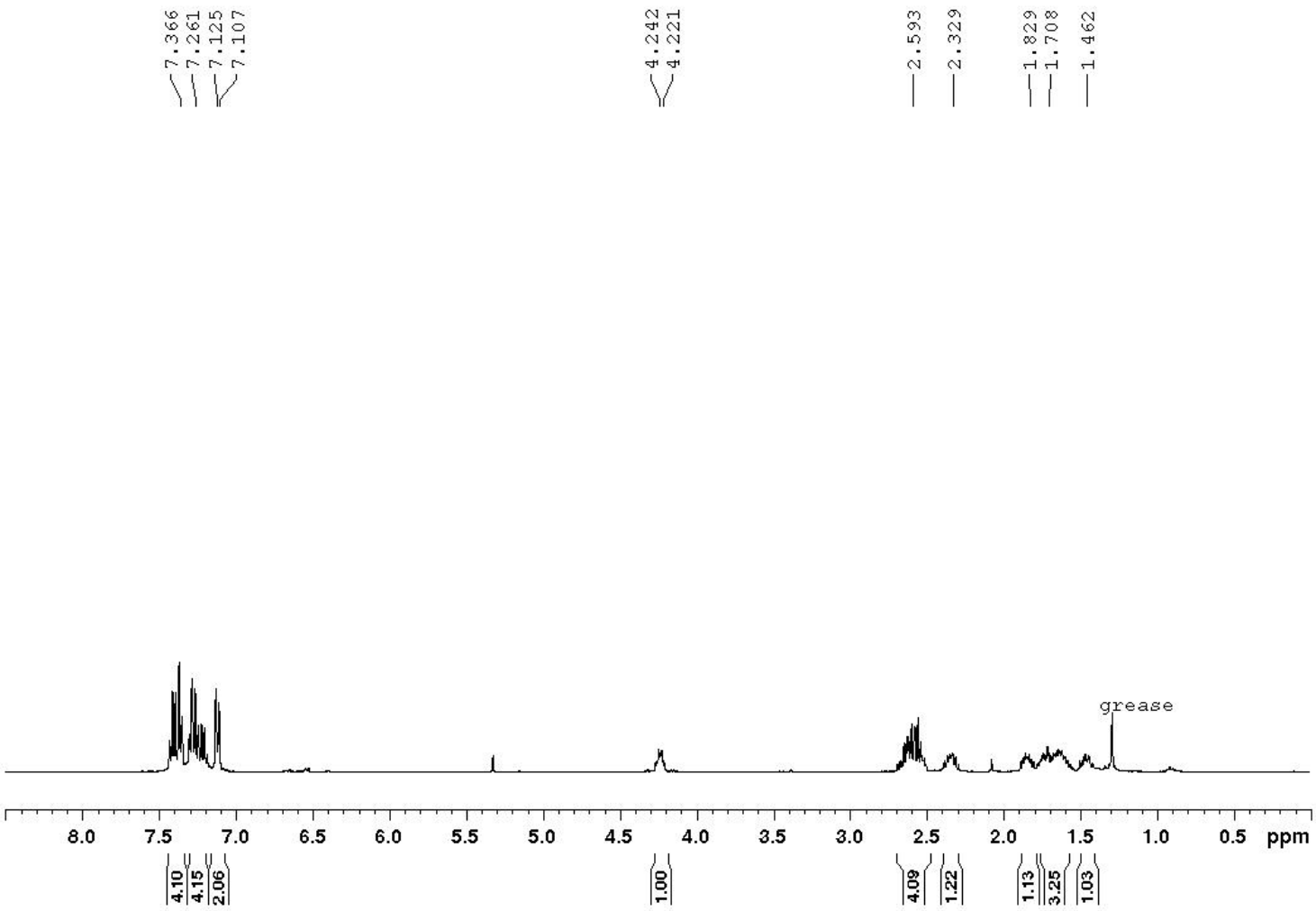


26

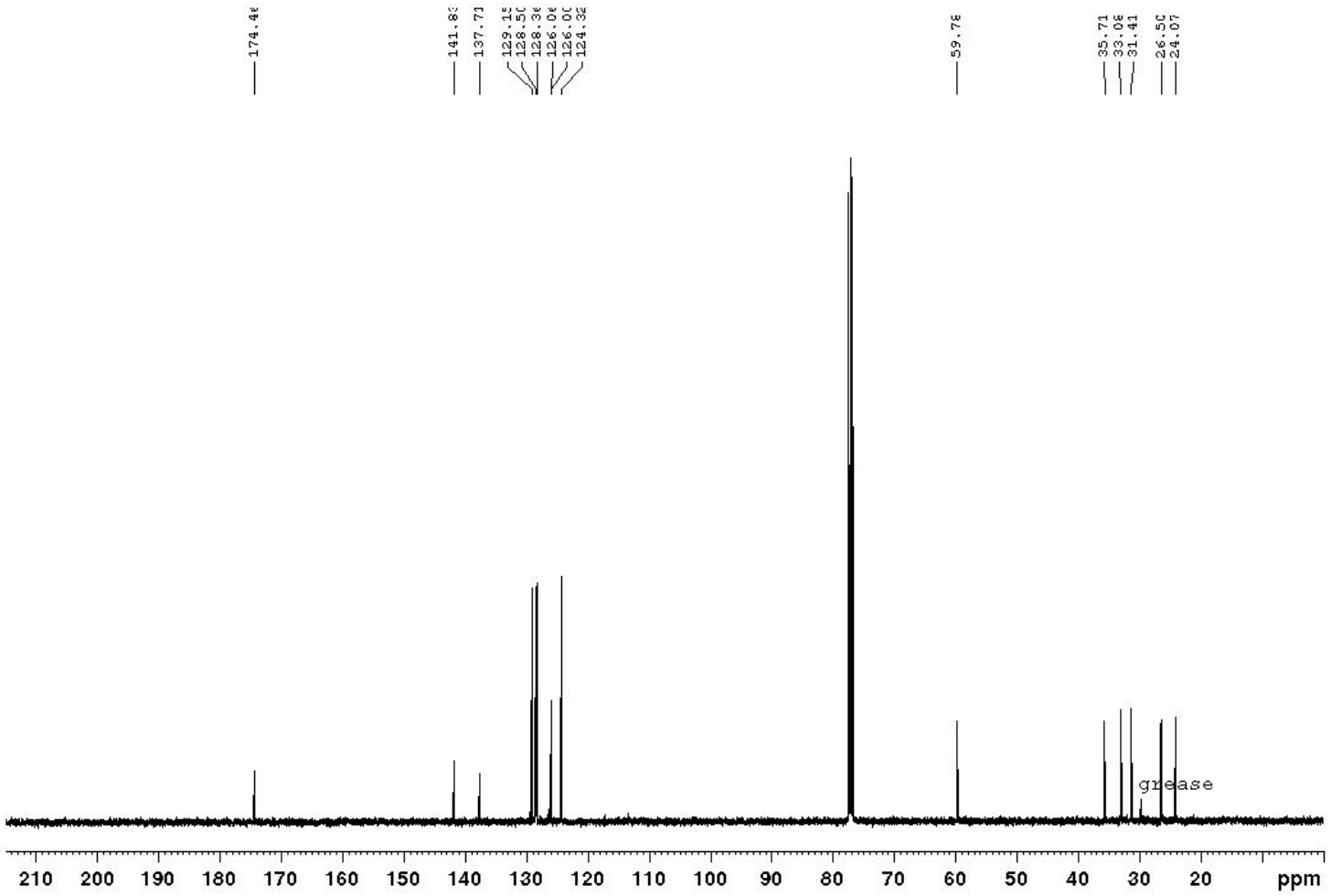


$[\alpha]_D^{20}$	+30.5° (*c* 0.74, $CHCl_3$)
TLC analysis	R_f 0.4 (40:60 hexanes:ethyl acetate)
HPLC analysis	Chiral HPLC analysis ((*S*,*S*)-WHELK-O 1, 100% isopropanol, flow rate = 1.0 mL/min) showed peaks at 9 minutes (5.5% (*R*)) and 17 minutes (94.5% (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.35–7.45 (4H, m, m,m',n,n'), 7.20–7.30 (4H, m, a,b,b',o), 7.12 (2H, d, *J* = 7.2 Hz, c.c'), 4.30–4.30 (1H, m, h), 2.50–2.70 (4H, m, e,j), 2.30–2.40 (1H, m, i), 1.80–1.90 (1H, m, i), 1.55–1.80 (3H, m, f,g), 1.40–1.50 (1H, m, g)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 174.46 (k), 141.83 (d), 137.71 (l), 129.15 (n,n'), 128.50 (b,b'), 128.36 (c,c'), 126.06 (o), 126.00 (a), 124.32 (m,m'), 59.78 (h), 35.71 (e), 33.08 (g), 31.41 (j), 26.50 (f), 24.07 (i)
IR (neat)	2933, 1690 (C=O stretch), 1596, 1496, 1388, 1292, 1220, 752, 693 cm^{-1}
HRMS (ESI)	$C_{19}H_{21}NNaO$ (M+Na): 302.1521, found 302.1534 *m/z*

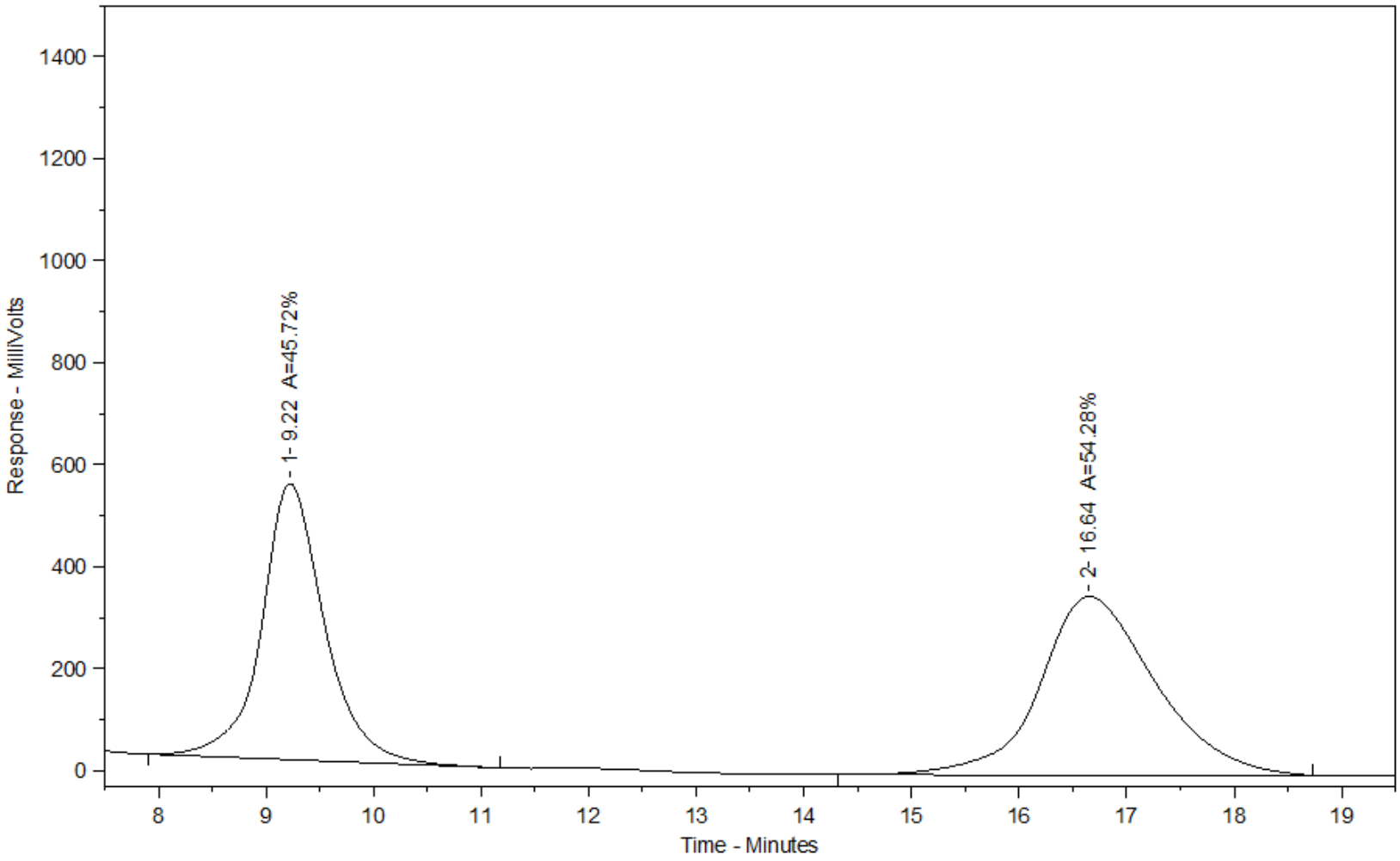
^{1}H NMR of 26


7.366
7.261
7.125
7.107
4.242
4.221
2.593
2.329
1.829
1.708
1.462
grease
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.10
4.15
2.06
1.00
4.09
1.22
1.13
3.25
1.03

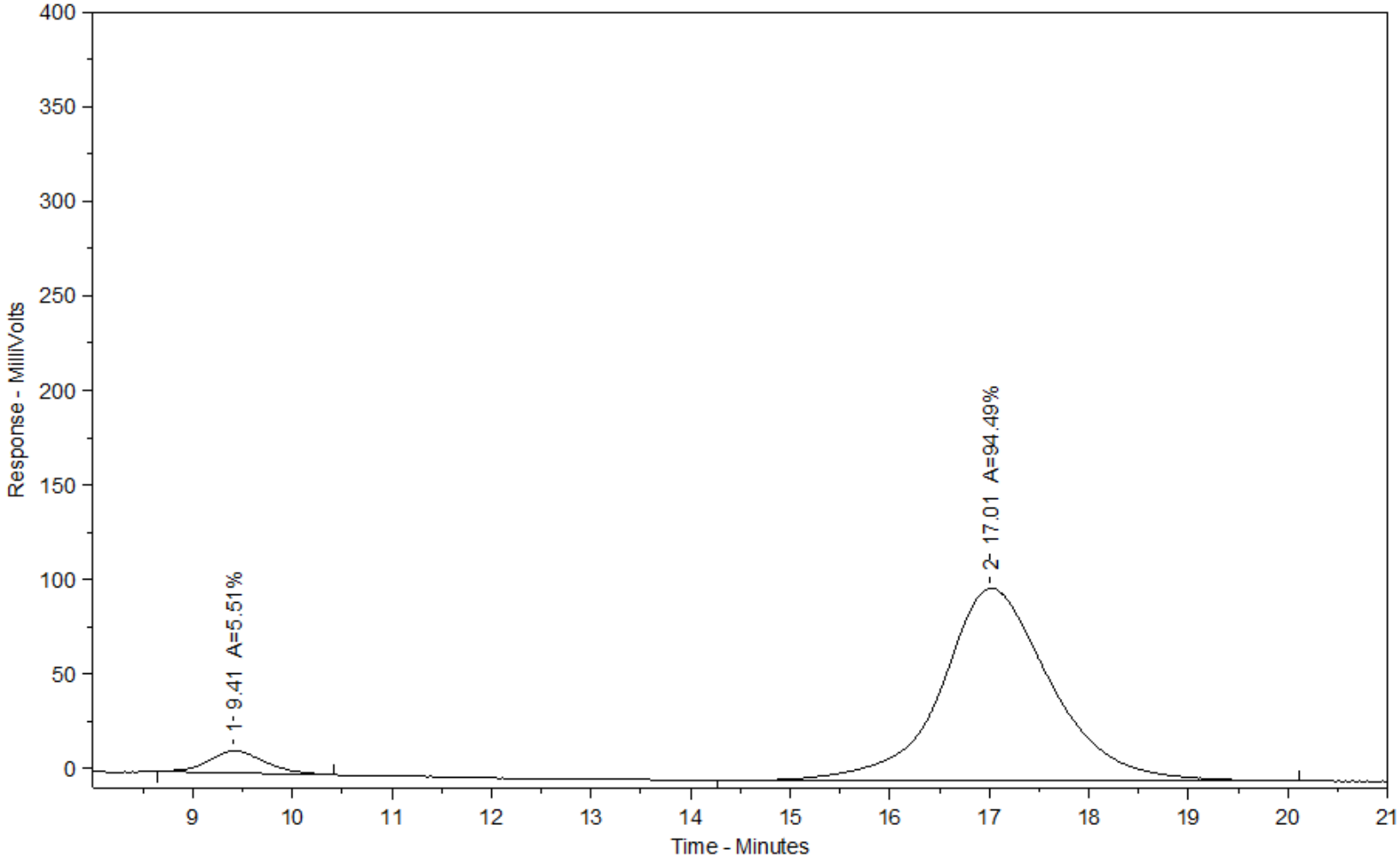
^{13}C NMR of 26


174.4
141.8
137.7
129.1
128.5
128.3
126.0
126.0
124.3
59.7
35.7
33.0
31.4
26.5
24.0
grease
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

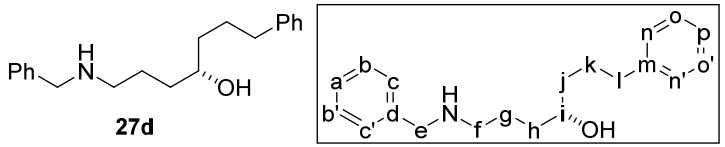
HPLC trace of 26



Racemic **26**



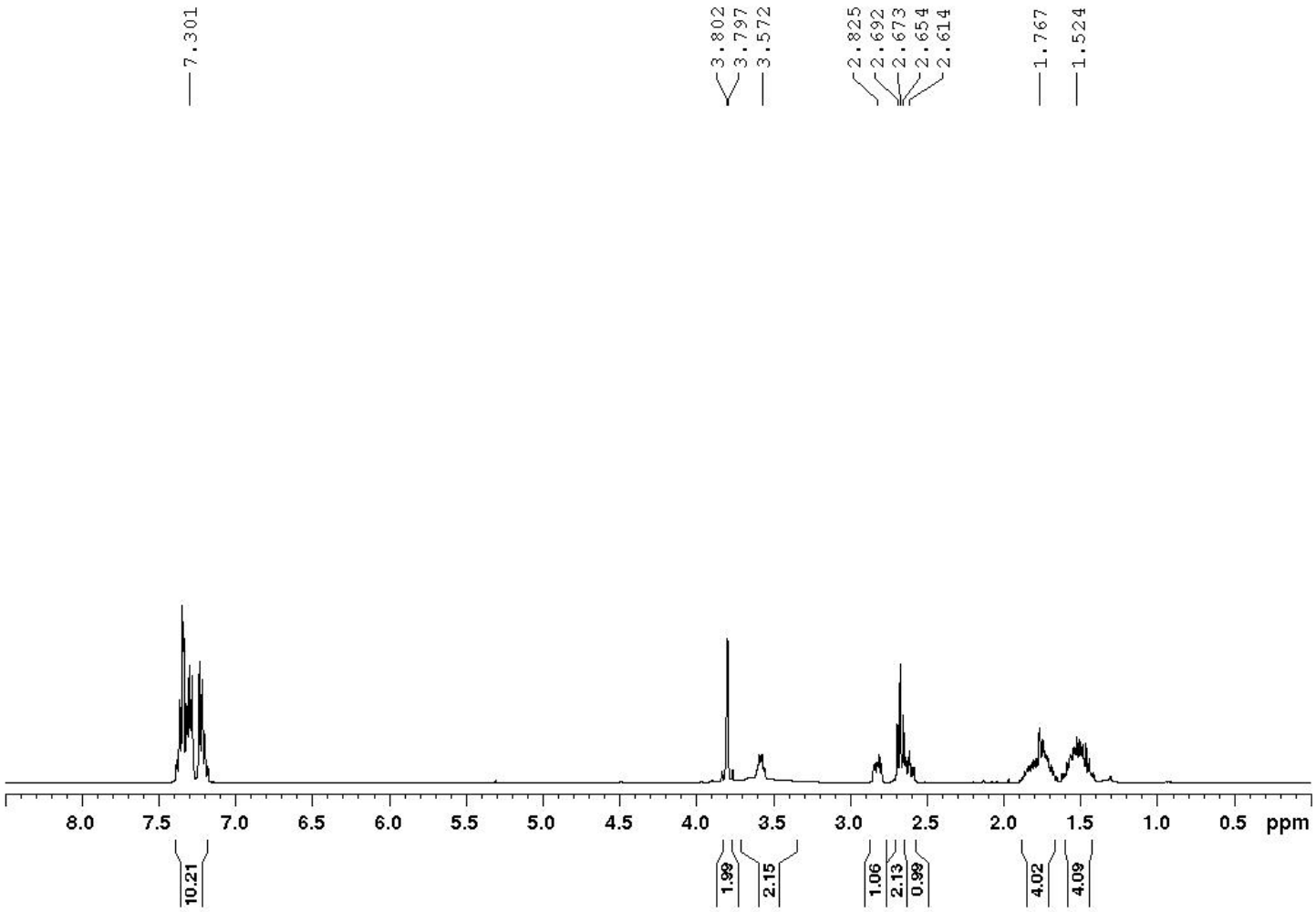
(*S*)-**26**



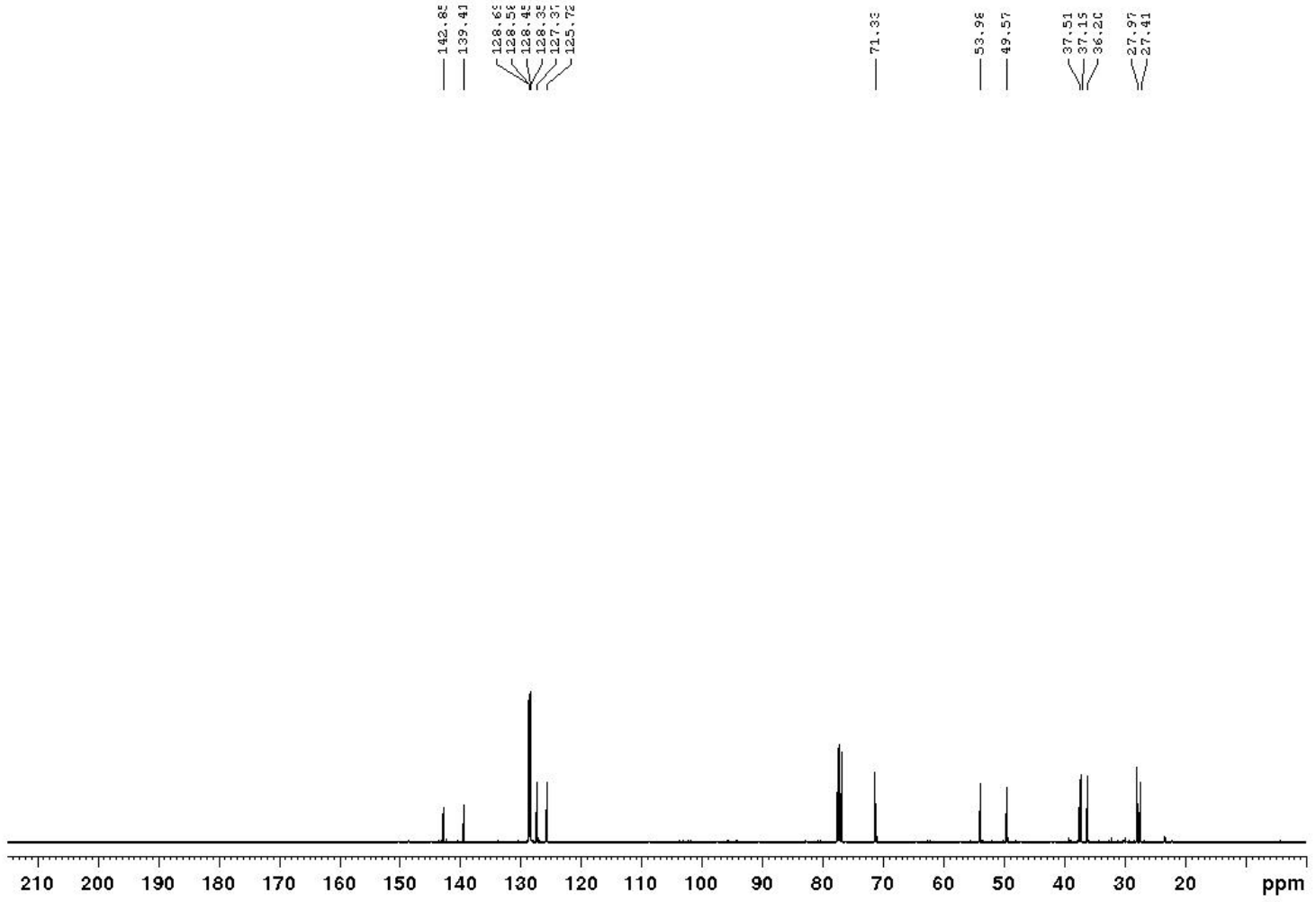
27d

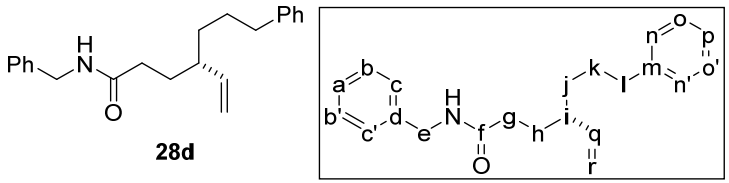
$[\alpha]_D^{20}$	+20.4º (*c* 2.0, $CHCl_3$)
m.p.	48.5–49.0 ºC
TLC analysis	0.2 (5:95 methanol:ethyl acetate)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.20–7.40 (10H, a,b,b',c,c',n,n',o,o',p), 3.80 (2H, d, *J* = 1.9 Hz, e), 3.40–3.70 (2H, m, i,OH), 2.75–2.85 (1H, m, f), 2.67 (2H, t, *J* = 7.7 Hz, l), 2.55–2.65 (1H, m, f), 1.65–1.90 (4H, m, h,k), 1.40–1.60 (4H, m, g,j)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 142.85 (m), 139.41 (d), 128.69 (b,b'), 128.58 (o,o'), 128.45 (n,n'), 127.35 (c,c'), 127.37 (a), 125.72 (p), 71.33 (i), 53.98 (e), 49.57 (f), 37.51 (j), 37.19 (h), 36.20 (l), 27.97 (k), 27.41 (g)
IR (neat)	3267 (N-H stretch, O-H stretch), 3084, 3026, 2868, 2827, 2813, 1495, 1451, 1363 (C-N stretch), 1346, 1118, 858, 734, 691 cm^{-1}
HRMS (ESI)	$C_{20}H_{27}NNaO$ (M+Na): 320.1990, found 320.1990 *m/z*

^{1}H NMR of 27d


7.301
3.802
3.797
3.572
2.825
2.692
2.673
2.654
2.614
1.767
1.524
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
10.21
1.99
2.15
1.06
2.13
0.99
4.02
4.09

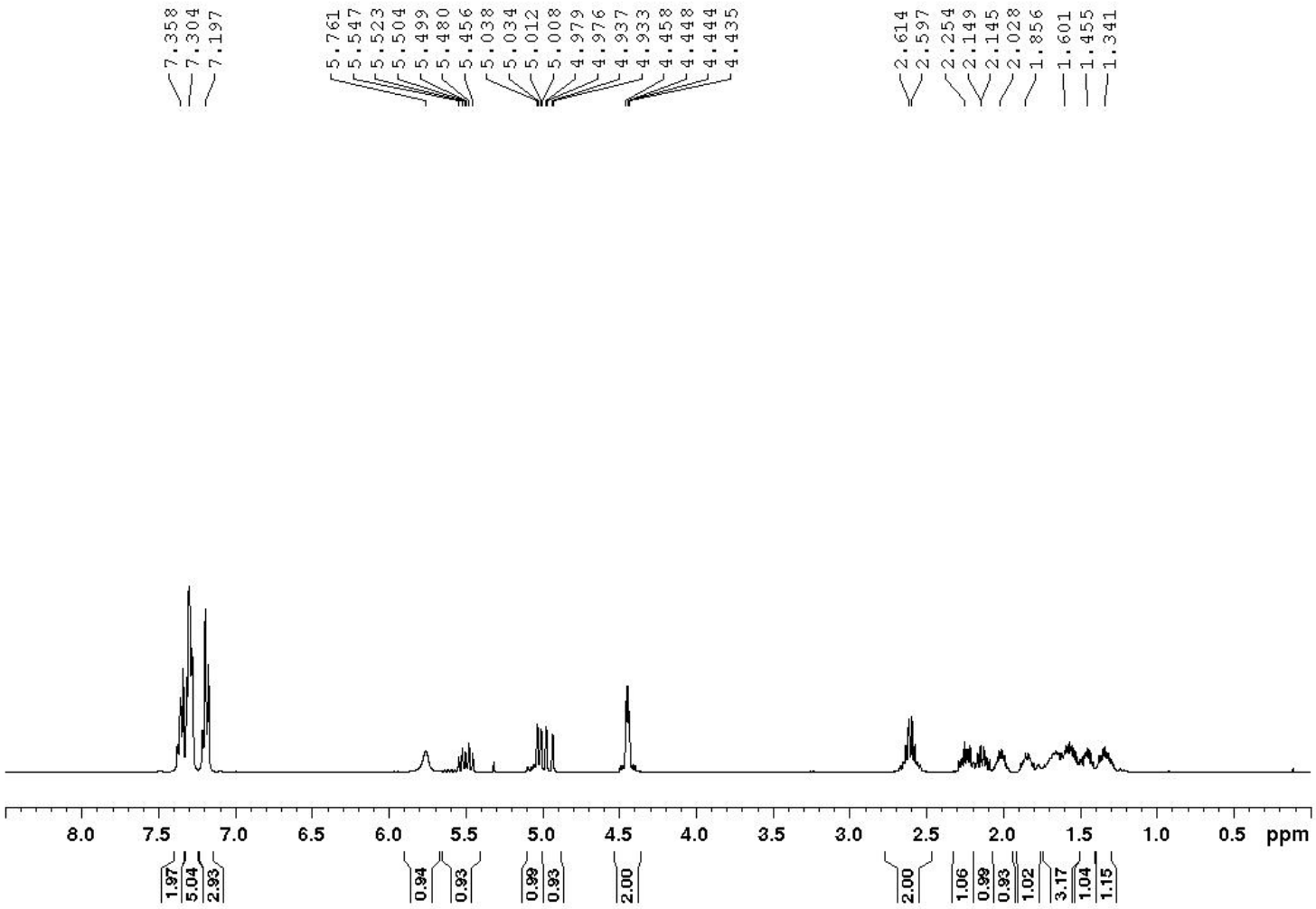
^{13}C NMR of 27d



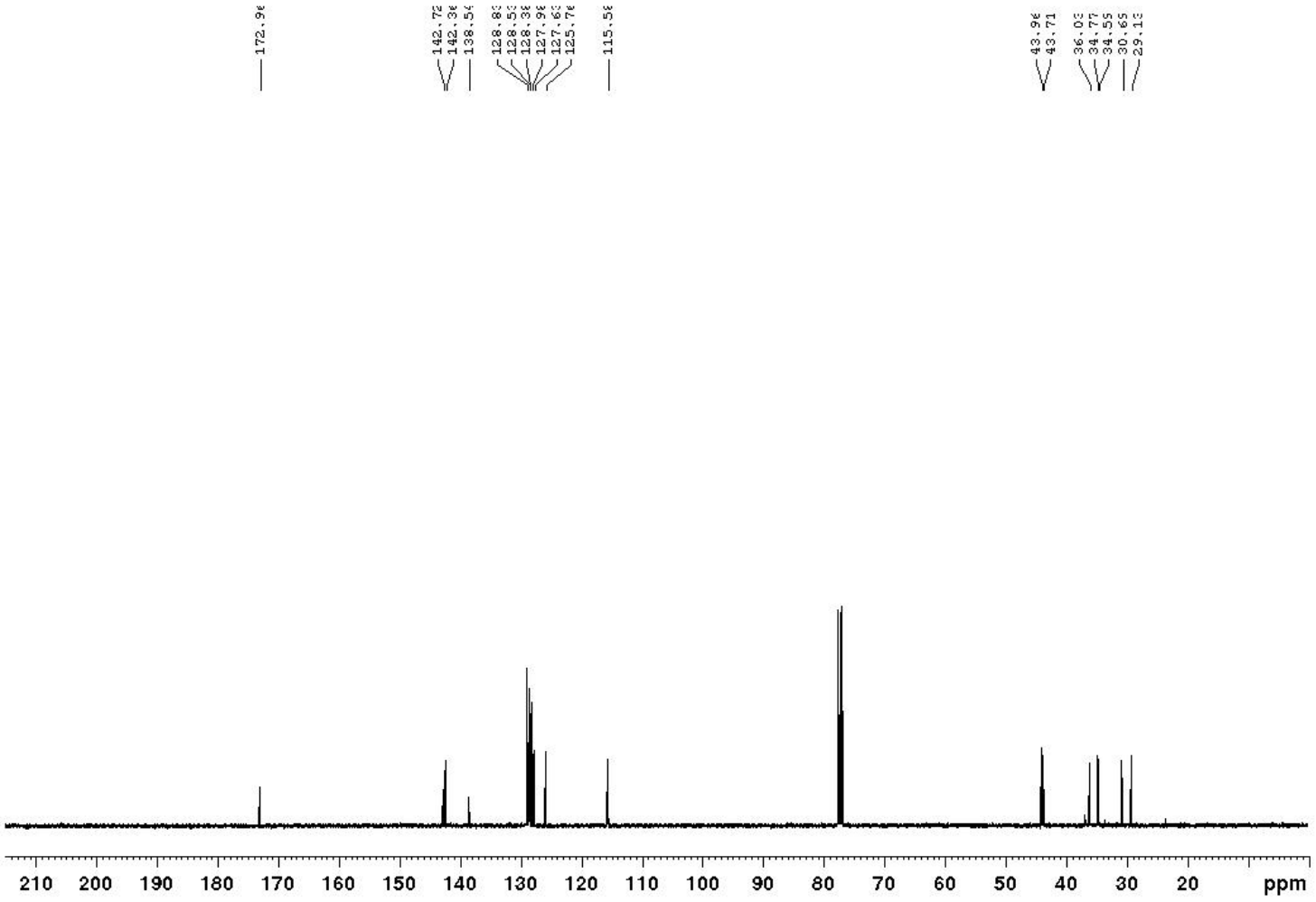


$[\alpha]_D^{20}$	–4.1° (*c* 2.0, $CHCl_3$)
TLC analysis	R_f 0.5 (50:50 hexanes:ethyl acetate)
HPLC analysis	Chiral HPLC analysis (Chiralcel-OJ-H, 90:10 hexanes:isopropanol, flow rate = 1.0 mL/min) showed peaks at 18 minutes (4.0% (*R*)) and 22 minutes (96.0% (*S*))
^{1}H NMR (400 MHz, $CDCl_3$)	7.35–7.40 (2H, m, b,b'), 7.25–7.35 (5H, a, n,n',o,o'), 7.15–7.25 (3H. c,c',p), 5.76 (1H, br s, NH), 5.50 (1H, dt, *J* = 17.0 and 9.6 Hz, q), 5.02 (1H, dd, *J* = 10.1 and 1.6 Hz, r), 4.96 (1H, dd, *J* = 17.1 and 1.5 Hz, r), 4.45 (2H, dd, *J* = 5.1 and 4.0 Hz, e), 2.50–2.70 (2H, m, l), 2.20–2.30 (1H, m, g), 2.10–2.20 (1H, m, g), 1.95–2.10 (1H, m, i), 1.80–1.90 (1H, m, k), 1.50–1.75 (3H, m, h,k), 1.40–1.50 (1H, m, j), 1.30–1.40 (1H, m, j)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 172.96 (f), 142.72 (q), 142.36 (m), 138.54 (d), 128.83 (o,o'), 128.53 (b,b'), 128.38 (n,n'), 127.98 (c,c') 127.63 (a), 125.76 (p), 115.58 (r), 43.96 (i), 43.71 (e), 36.03 (l), 34.77 (j), 34.59 (g), 30.69 (k), 29.13 (h)
IR (neat)	3275 (N-H stretch), 3063, 3027, 2925, 2856, 1641 (C=O stretch), 1541, 1495, 1453, 911, 745, 696 cm^{-1}
HRMS (ESI)	$C_{22}H_{27}NNaO$ (M+Na): 344.1990, found 344.1996 *m/z*

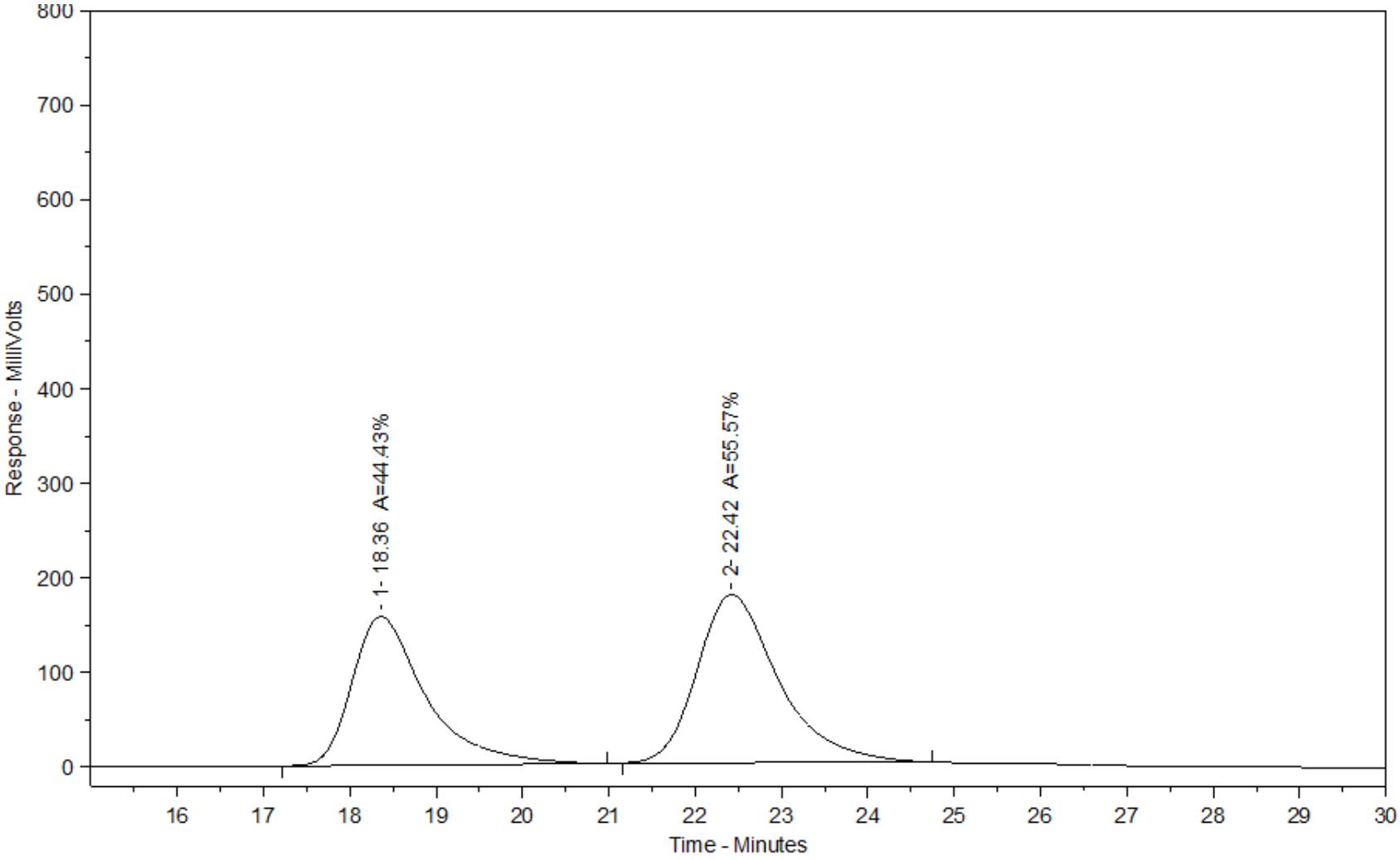
^{1}H NMR of 28d


7.358
7.304
7.197
5.761
5.547
5.523
5.504
5.499
5.480
5.456
5.038
5.034
5.012
5.008
4.979
4.976
4.937
4.933
4.458
4.448
4.444
4.435
2.614
2.597
2.254
2.149
2.145
2.028
1.856
1.601
1.455
1.341
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.97
5.04
2.93
0.94
0.93
0.99
0.93
2.00
2.00
1.06
0.99
0.93
1.02
3.17
1.04
1.15

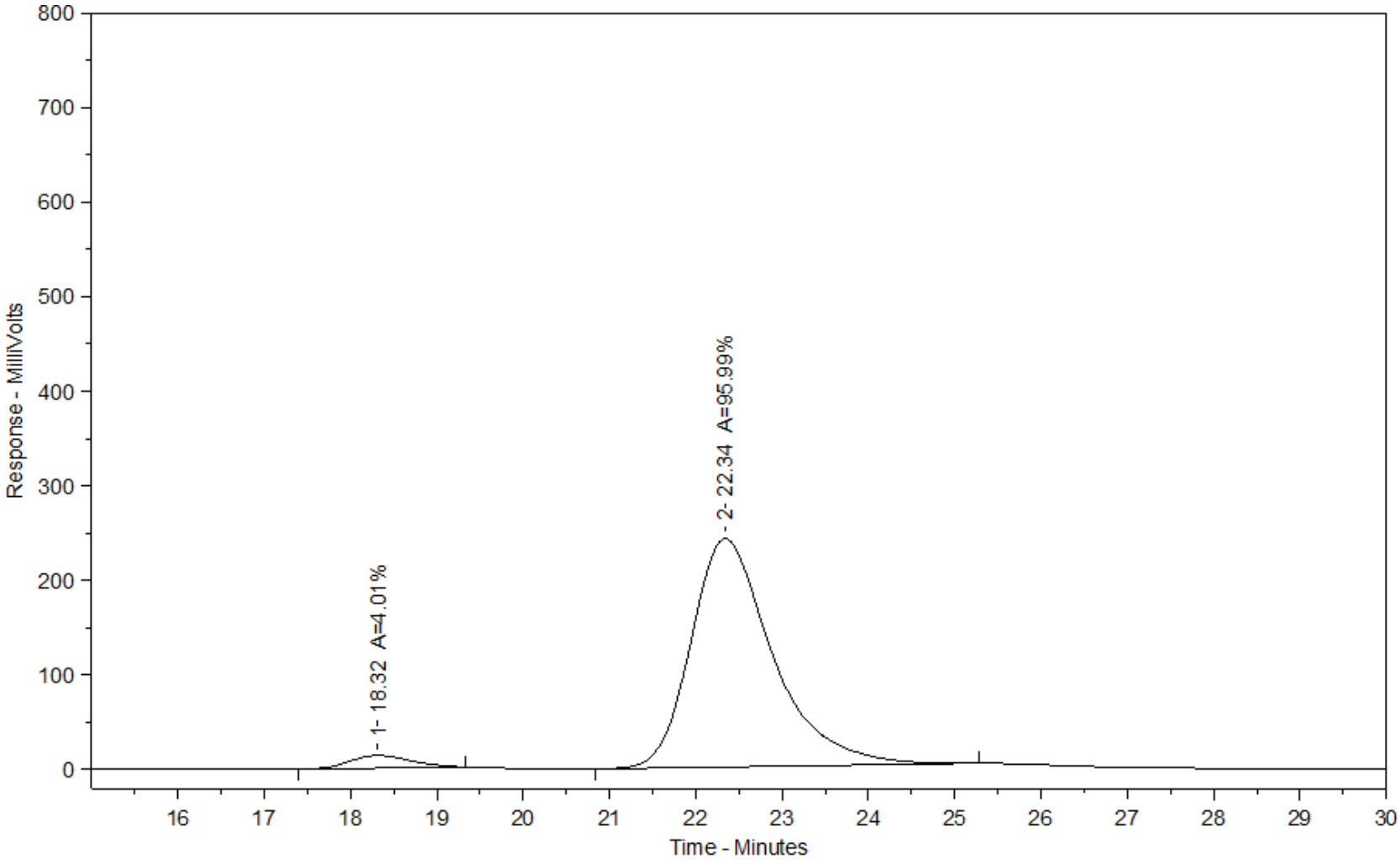
^{13}C NMR of 28d



HPLC trace of 28d



Racemic **28d**



(*S*)-**28d**