Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

(7,8-Dicarba-*nido*-undecaboran-7-yl)acetic acid: synthesis of individual enantiomers and the first example of determination of absolute configuration of chiral *nido*-carborane

Dmitry A. Gruzdev,* Angelina A. Telegina, Evgeny N. Chulakov, Galina L. Levit and Victor P. Krasnov

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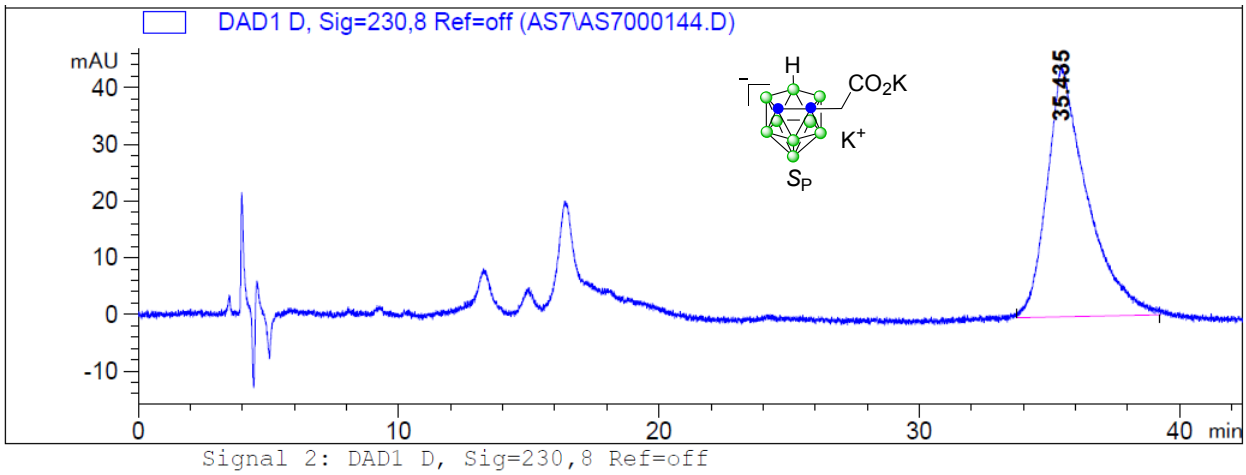
1. Configuration assignment of *nido*-carborane derivatives

Benzyl (S_P)-(*nido*-carboranyl)acetate, caesium salt [(S_P)-11-Cs]. Caesium fluoride (0.77 mg, 5.04 mmol) and HCl conc. (0.28 mL, 3.36 mmol) were added to a solution of benzyl (R_P)-(3-amino-*closo*-carboran-1-yl)acetate [(R_P)-**9**][S1] (0.52 g, 1.68 mmol) in BnOH (17 mL). The reaction mixture was stirred at 80 °C for 12 h. EtOAc (40 mL) was added and the solution was washed with H_2O (3 × 25 mL). Organic layer was evaporated to dryness under reduced pressure. The residue was subjected to flash column chromatography (eluent CH_2Cl_2–EtOH from 95 : 5 to 8 : 2) to afford compound (S_P)-**11-Cs** as a slow eluting component. Yield 97.8 mg (14%). Hygroscopic semisolid. NMR spectra were identical to those of compound **11-K** (see the Experimental section). HRMS ESI(−), *m*/*z* calcd for $C_{11}H_{20}{}^{11}B_9O_2$ [M – Cs]$^-$: 283.2323, found 283.2322.

(S_P)-(*nido*-Carboranyl)acetic acid, potassium Salt [(S_P)-1-K]. Concentrated HCl (2.7 mL) was added to a solution of compound (S_P)-**11-Cs** (93 mg, 0.22 mmol) in AcOH (2.7 mL). The mixture was heated at 102-105 °C for 15 h, then evaporated to dryness under reduced pressure. 4 N HCl (7 mL) was added to the residue and the mixture was extracted with Et_2O (3 × 10 mL). Organic layers were washed with 4 N HCl (10 mL), dried with Na_2SO_4 and evaporated to dryness under reduced pressure. The residue was dissolved in ethanolic solution of KOH (0.85 N, 1.2 mL). The resulting solution was filtered, then an excess of solid CO_2 was added. The precipitate was filtered off and the filtrate was evaporated to dryness under reduced pressure. Yield 60.1 mg (99%). Hygroscopic semisolid. NMR spectra were identical to those of compound (R_P)-**1-K** obtained starting from compound (*S*,R_P)-**7a** (see the Experimental section). $[\alpha]_D^{20}$ −5.0 (*c* 0.23, acetone–MeOH 4 : 1). HPLC (*S*,*S*-Whelk O1, MeOH–H_2O–AcOH–Et_3N 40.00 : 59.90 : 0.05 : 0.05, 0.75 mL/min): τ 35.48 min. HRMS ESI(−), *m*/*z* calcd for $C_4H_{14}{}^{11}B_9O_2$ [M – 2K + H]$^-$: 193.1837, found 193.1838.



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Totals :				4751.17480	44.07985	

Figure S1 HPLC chromatogram of compound (S_P)-(−)-**1-K** obtained from the known compound (R_P)-**9**

[S1] D. A. Gruzdev, V. O. Ustinova, E. N. Chulakov, V. A. Ol'shevskaya, G. L. Levit, P. A. Slepukhin, V. P. Krasnov and V. N. Charushin, *J. Organomet. Chem.*, 2018, **876**, 50–56.

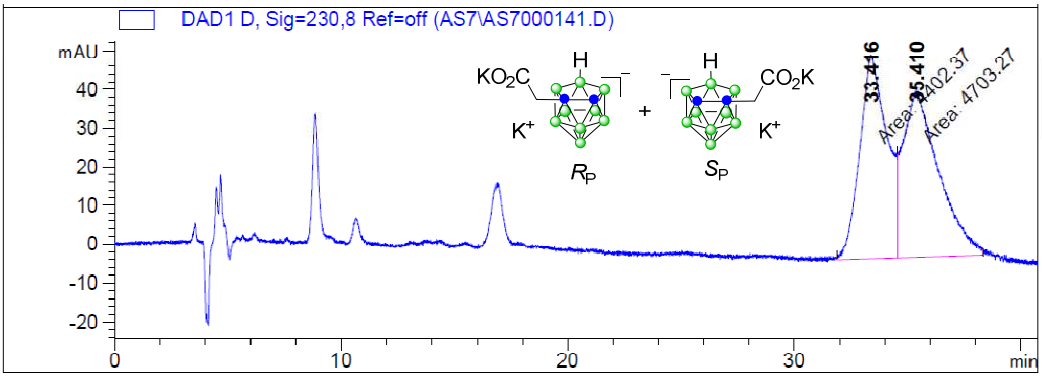

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Figure S2 HPLC chromatogram of racemic compound **1-K**

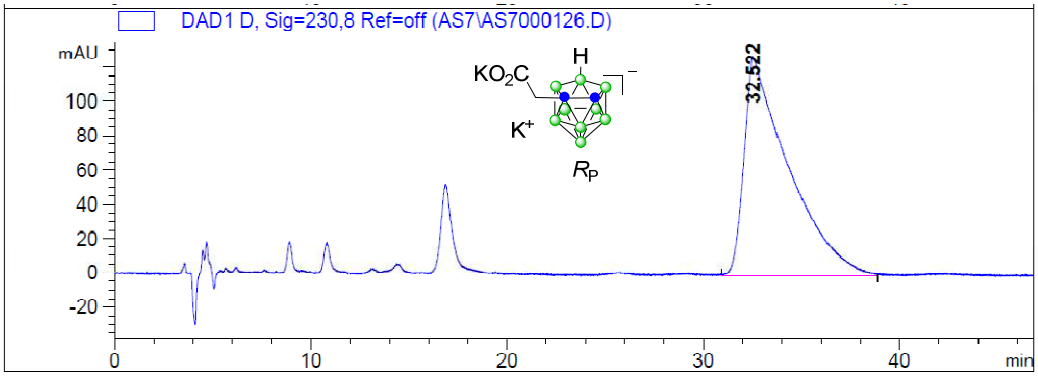


Figure S3 HPLC chromatogram of compound (R_P)-(+)-**1-K** obtained from amide (S,R_P)-**7a**

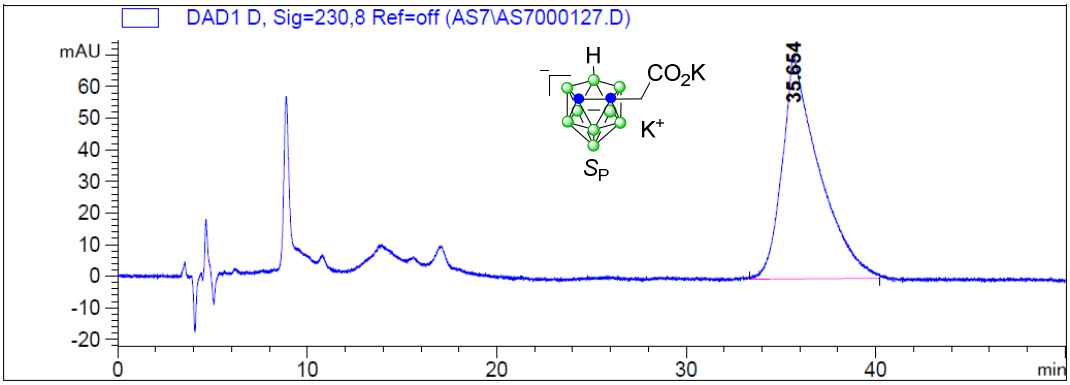
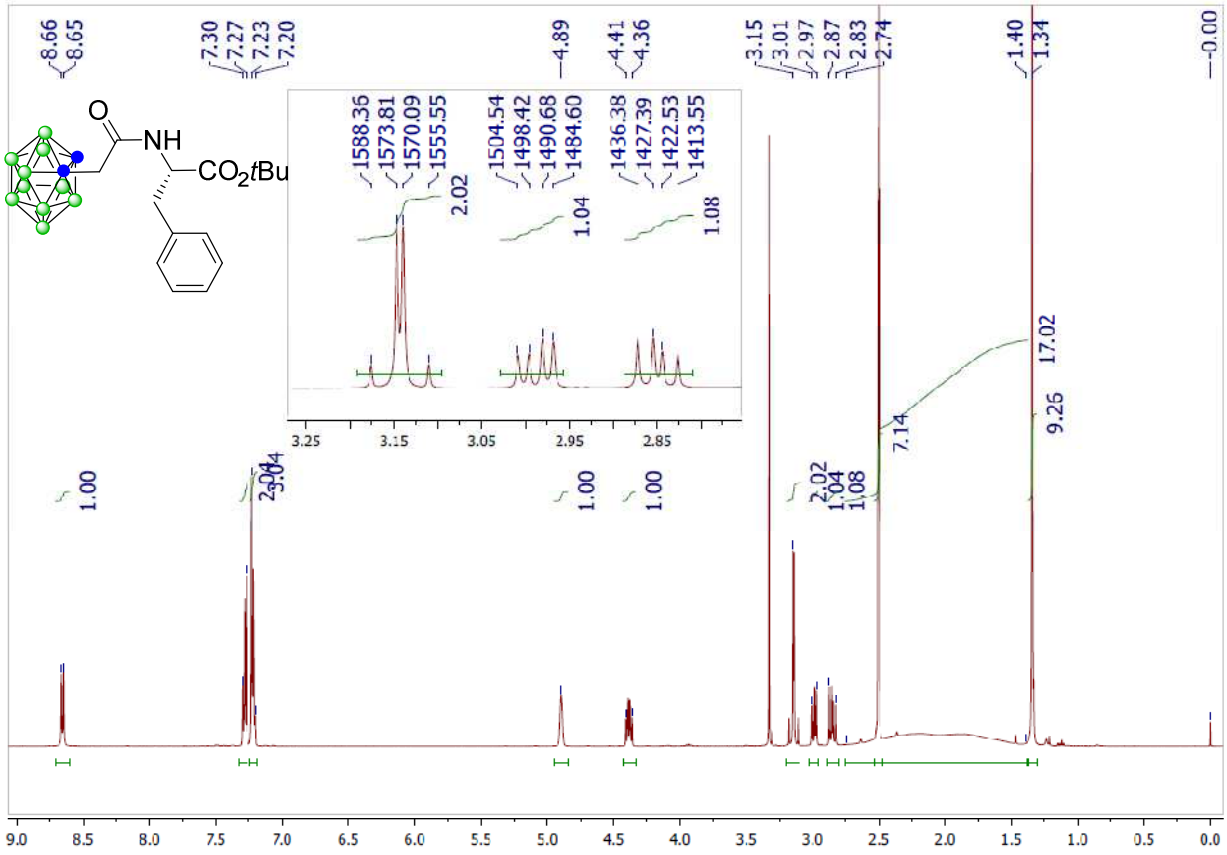
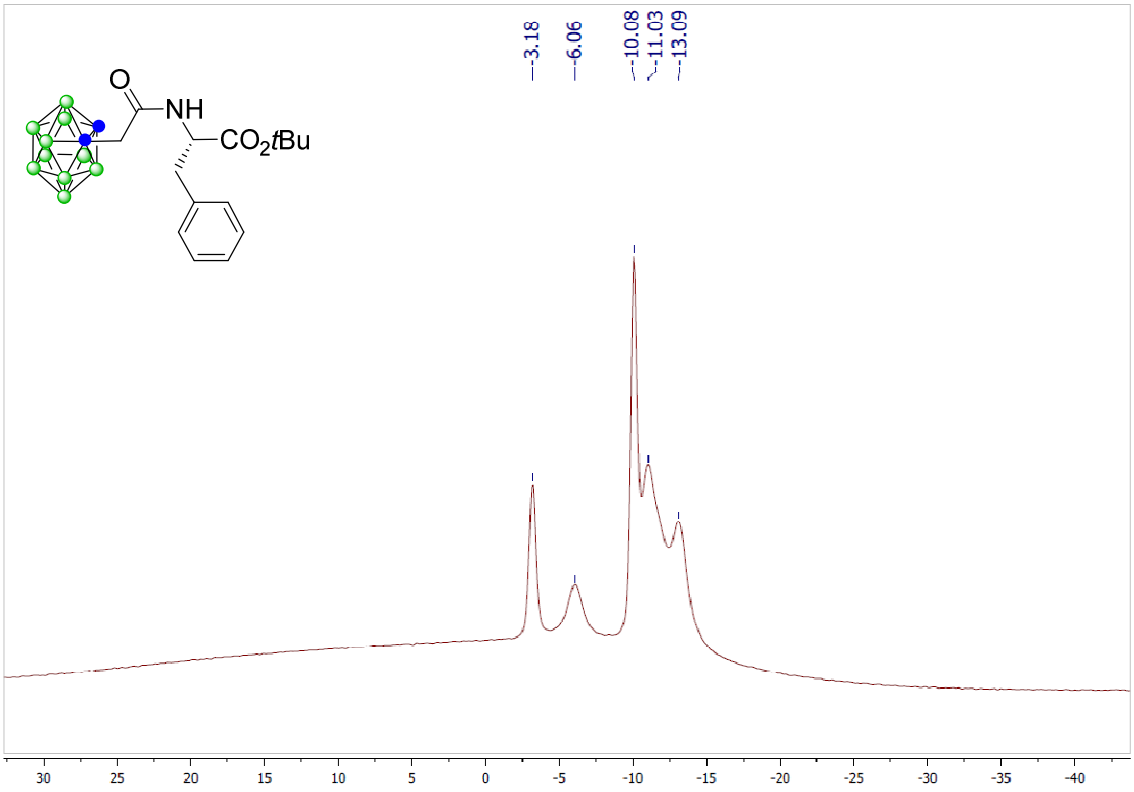


Figure S4 HPLC chromatogram of compound (S_P)-(−)-**1-K** obtained from amide (S,S_P)-**7a**

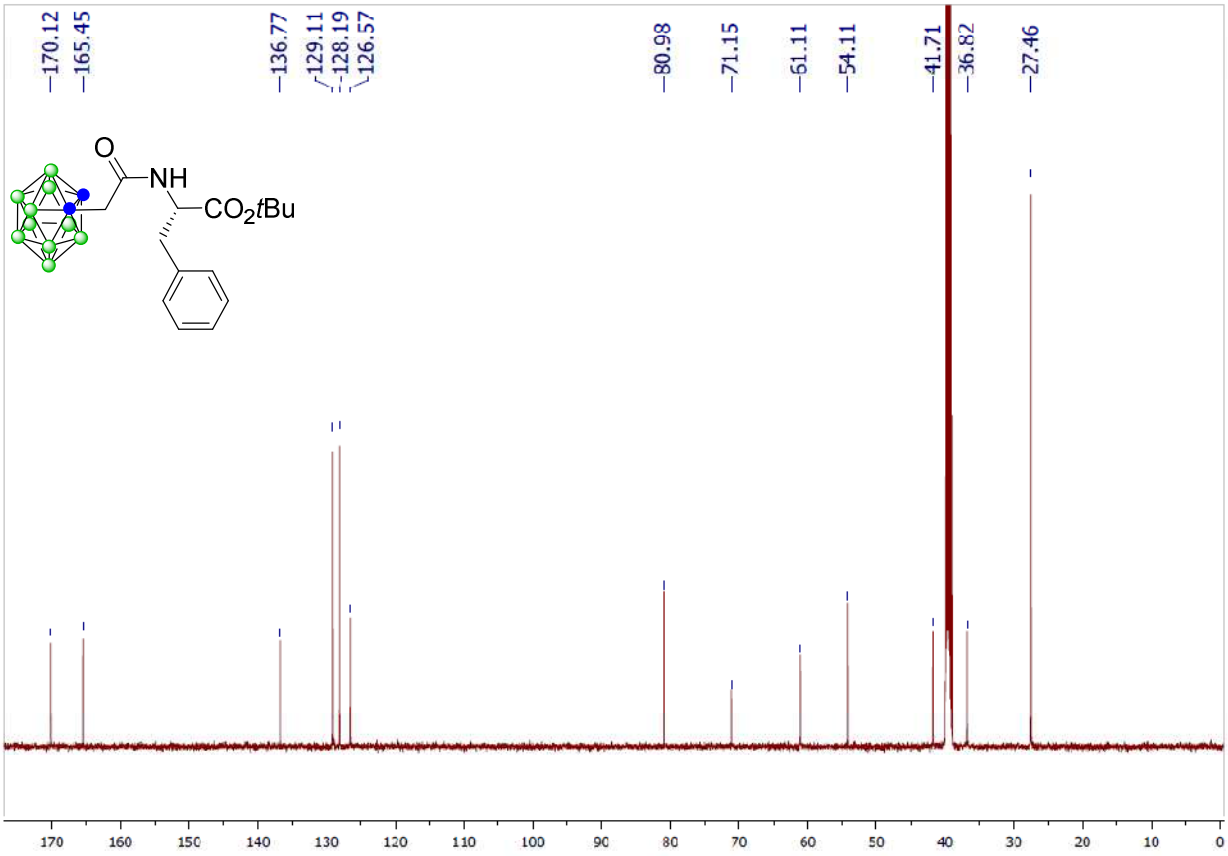
2. NMR spectra



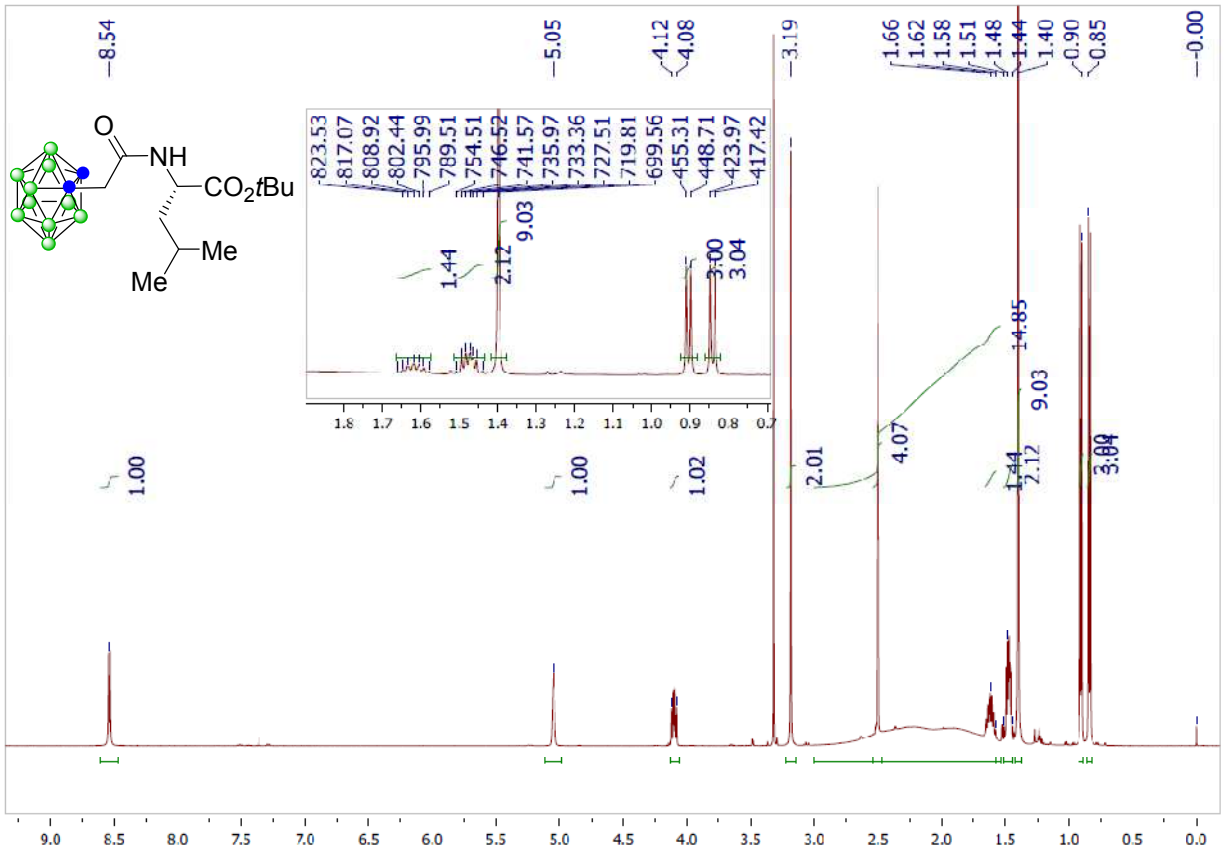
^{1}H NMR spectrum of compound **3a** (DMSO-d_6, 25 °C, 500 MHz)



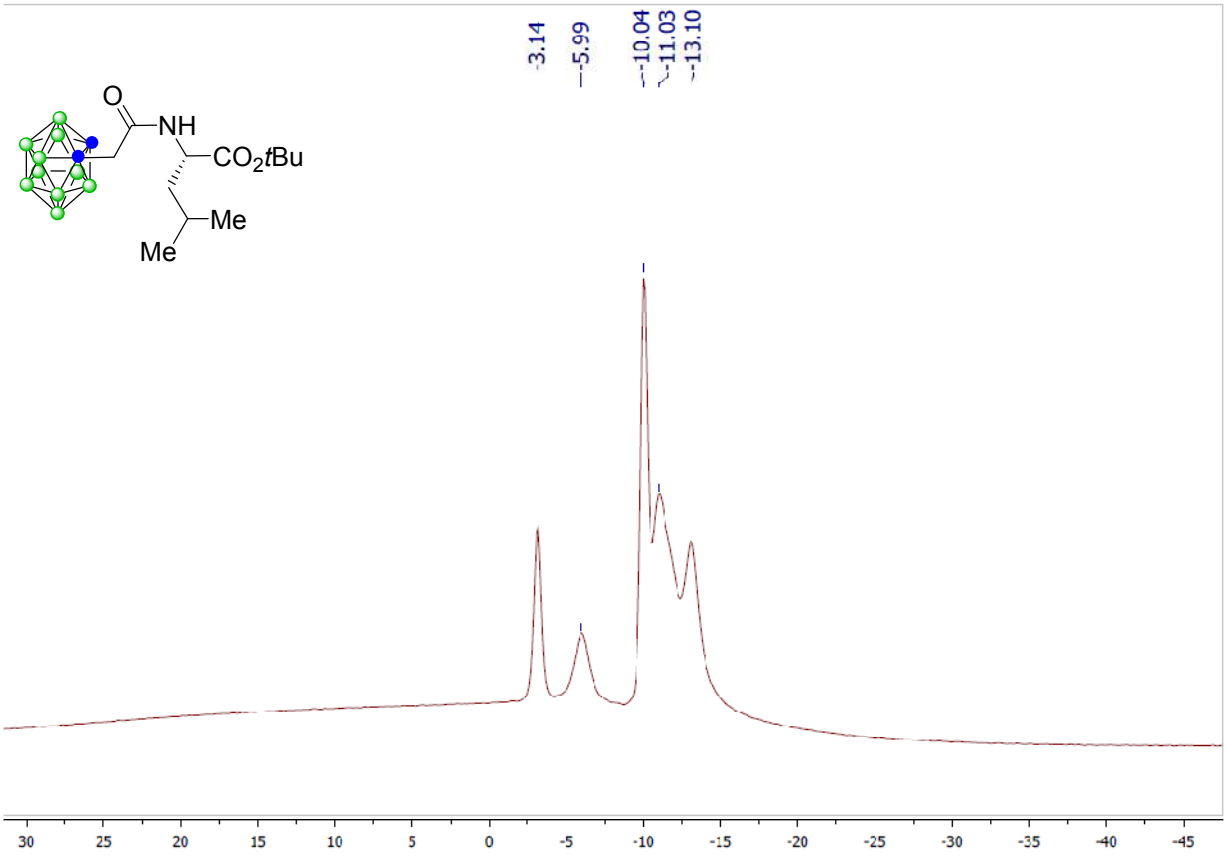
^{11}B{^{1}H} NMR spectrum of compound **3a** (DMSO-d_6, 25 °C, 160 MHz)



$^{13}C\{^{1}H\}$ NMR spectrum of compound **3a** (DMSO-d_6, 25 °C, 126 MHz)



^{1}H NMR spectrum of compound **3b** (DMSO-d_6, 25 °C, 500 MHz)



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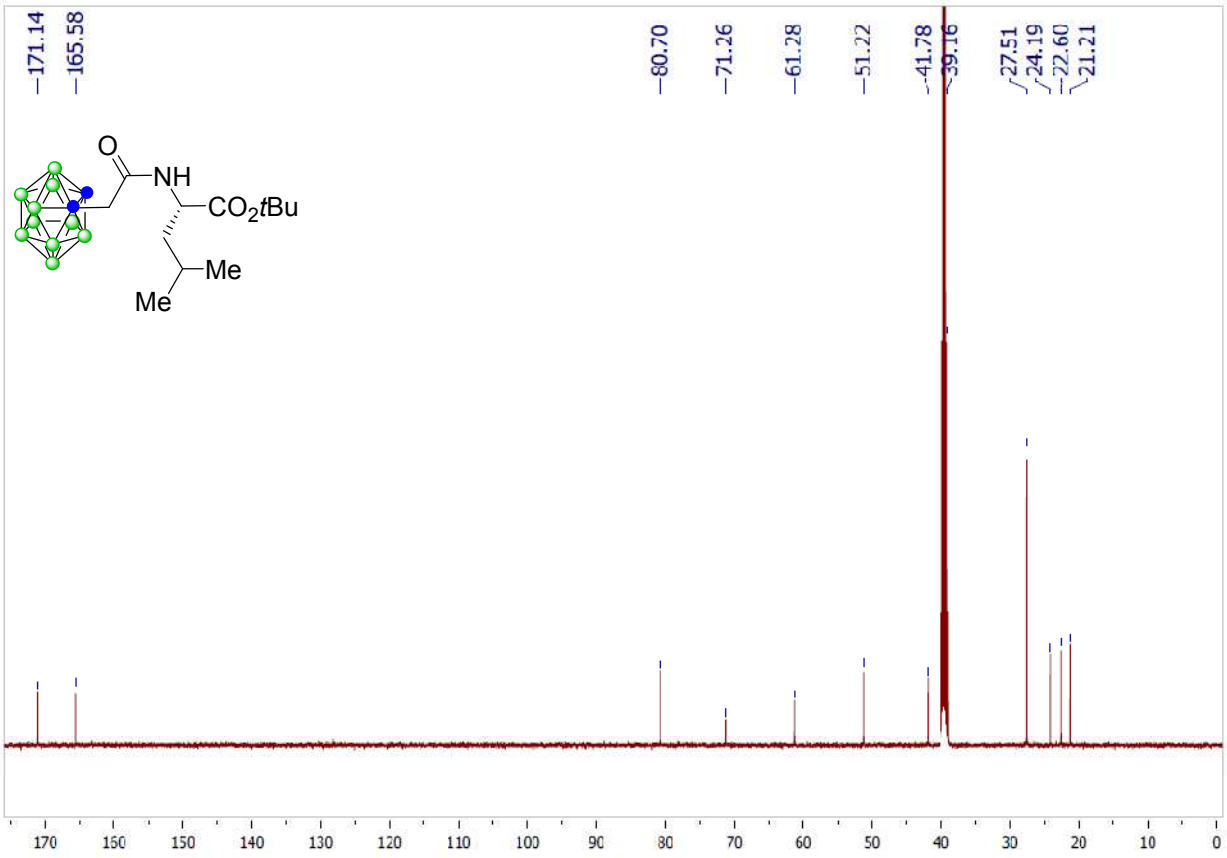

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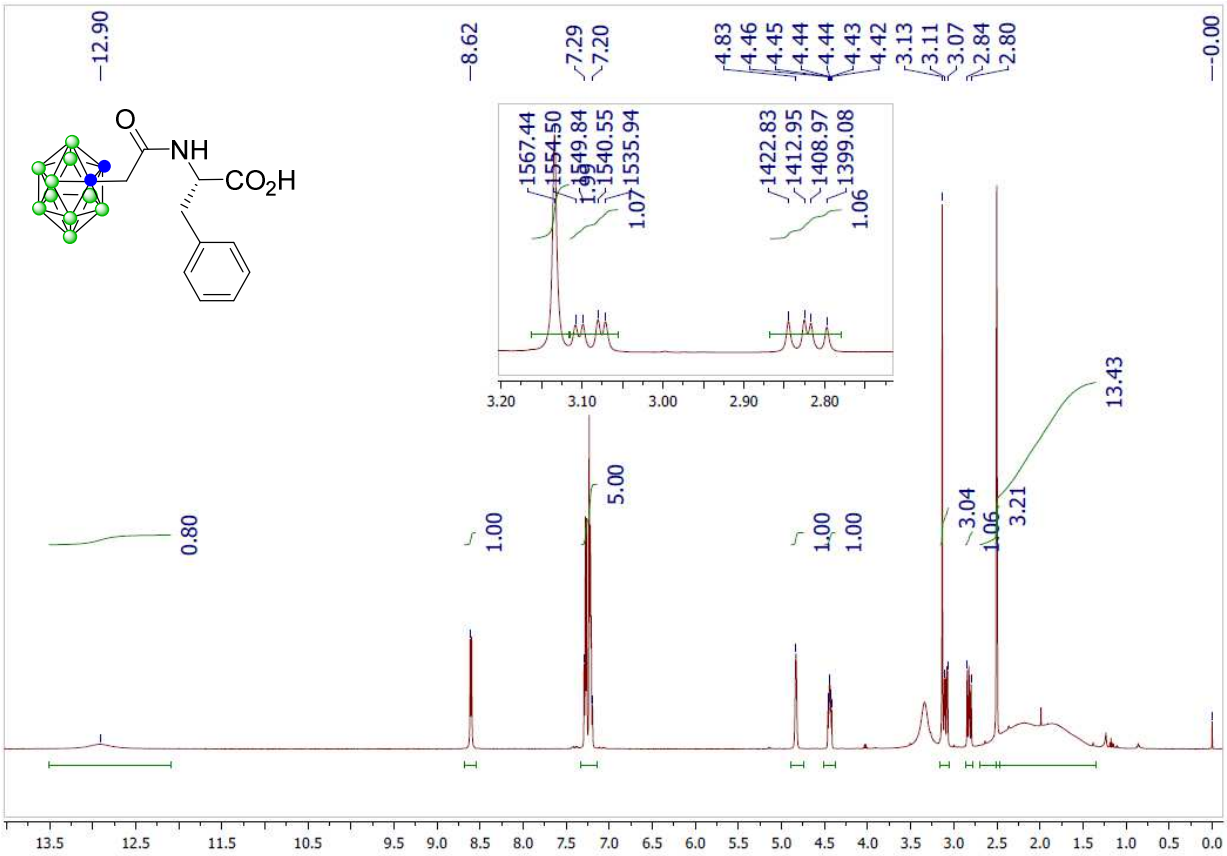

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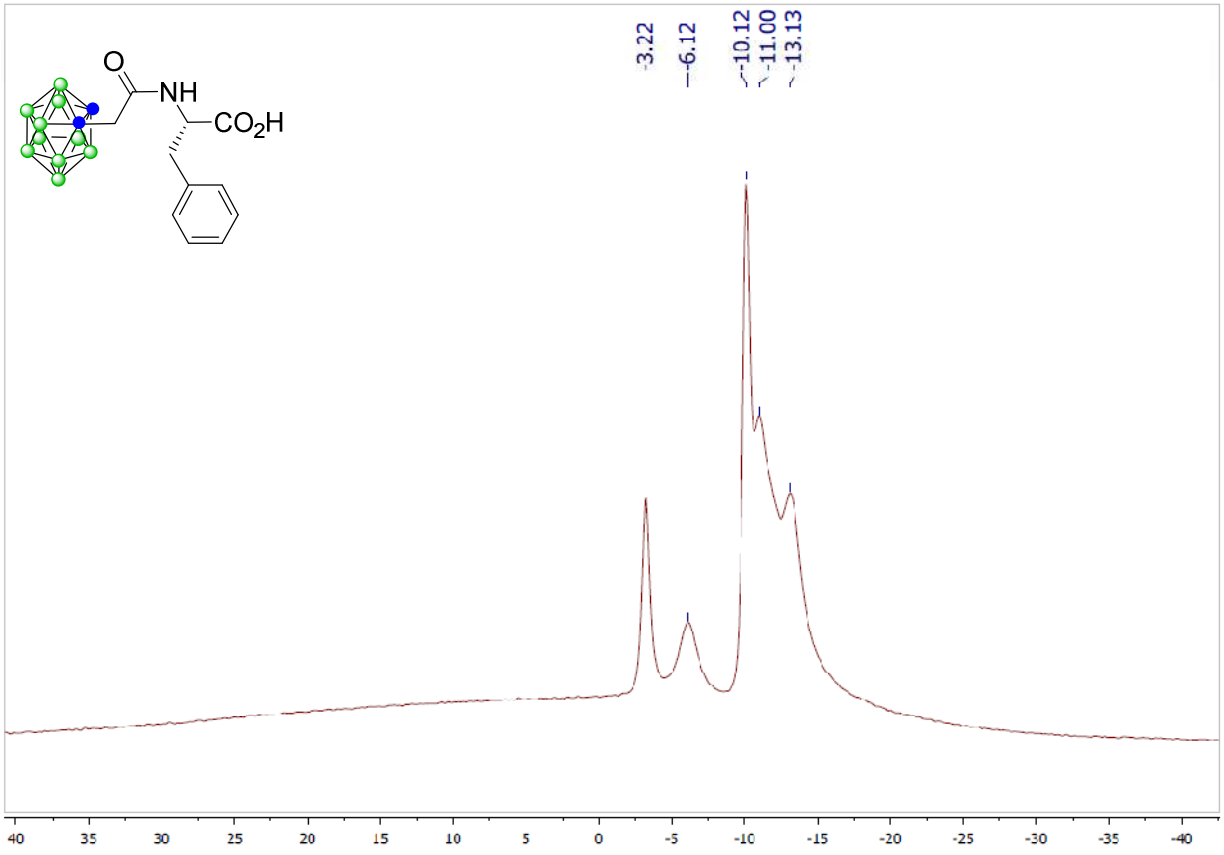

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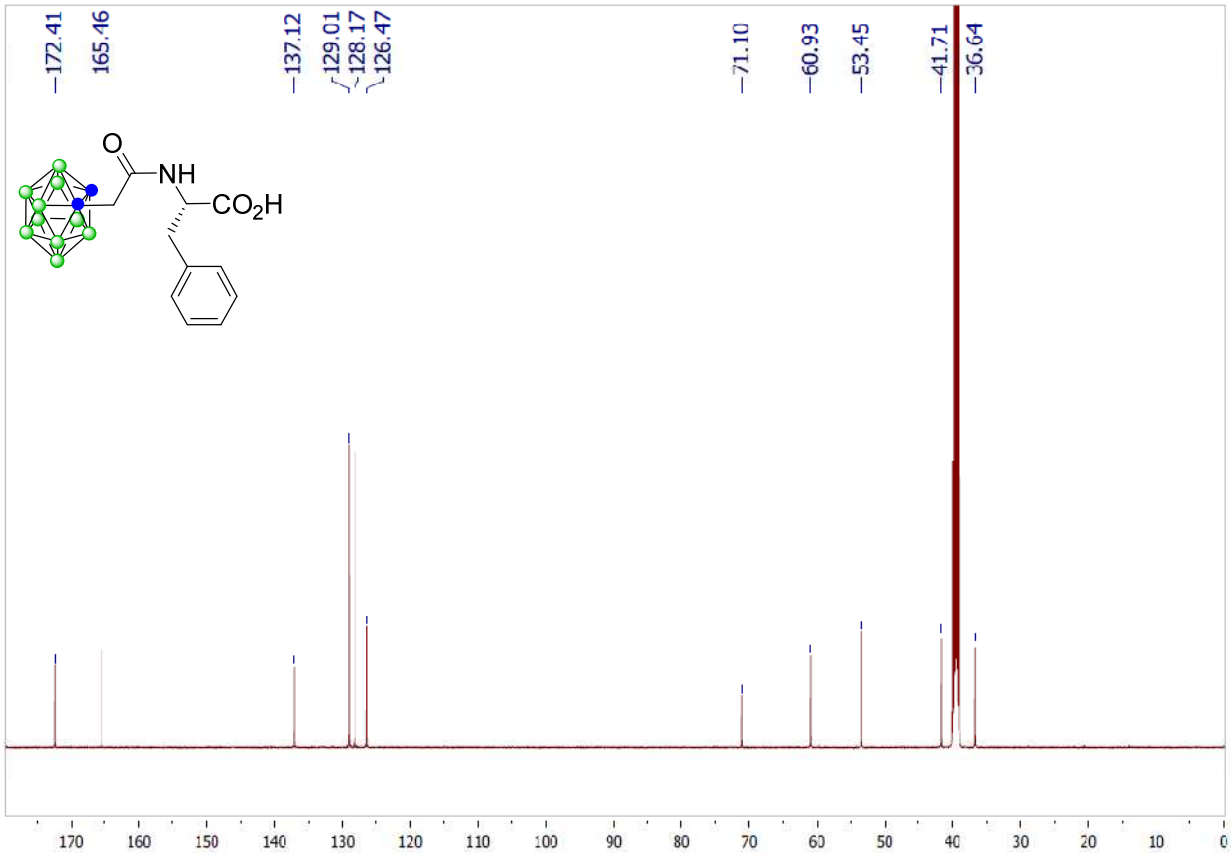

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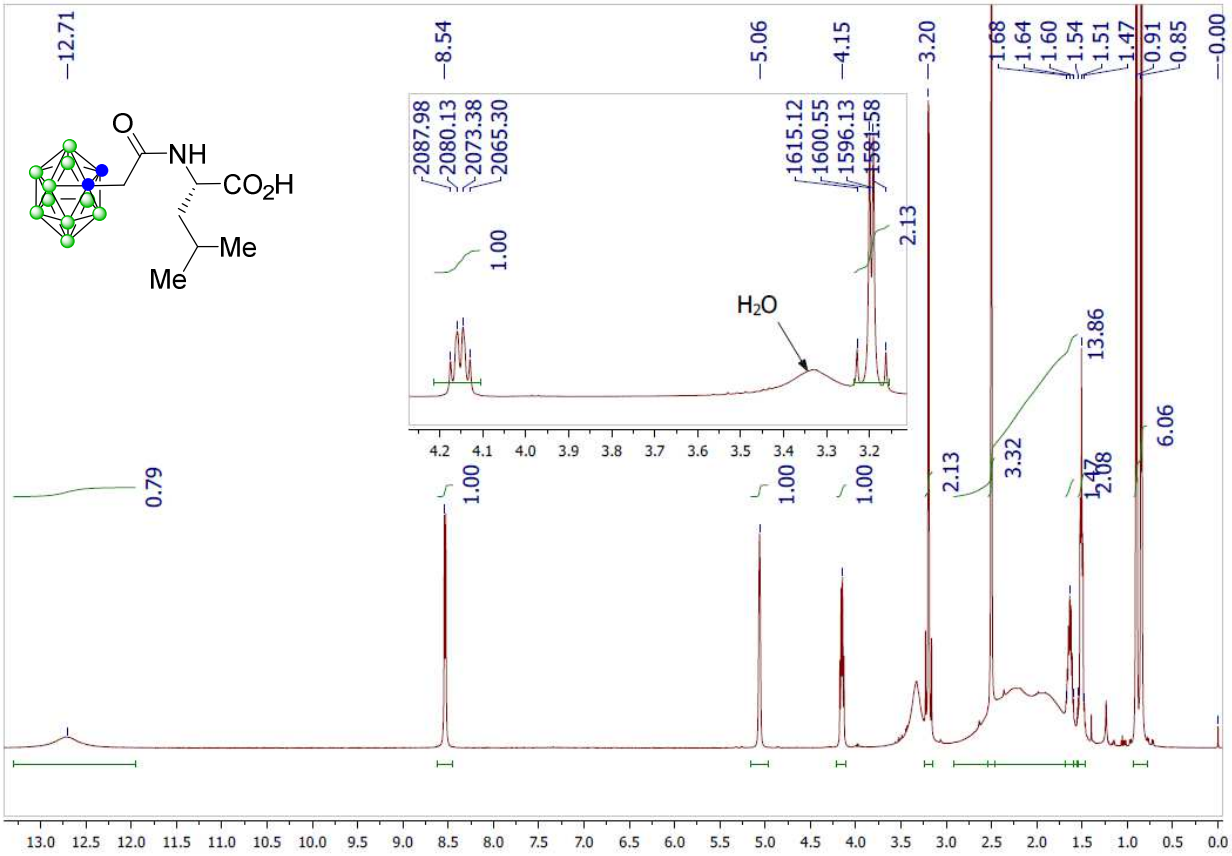

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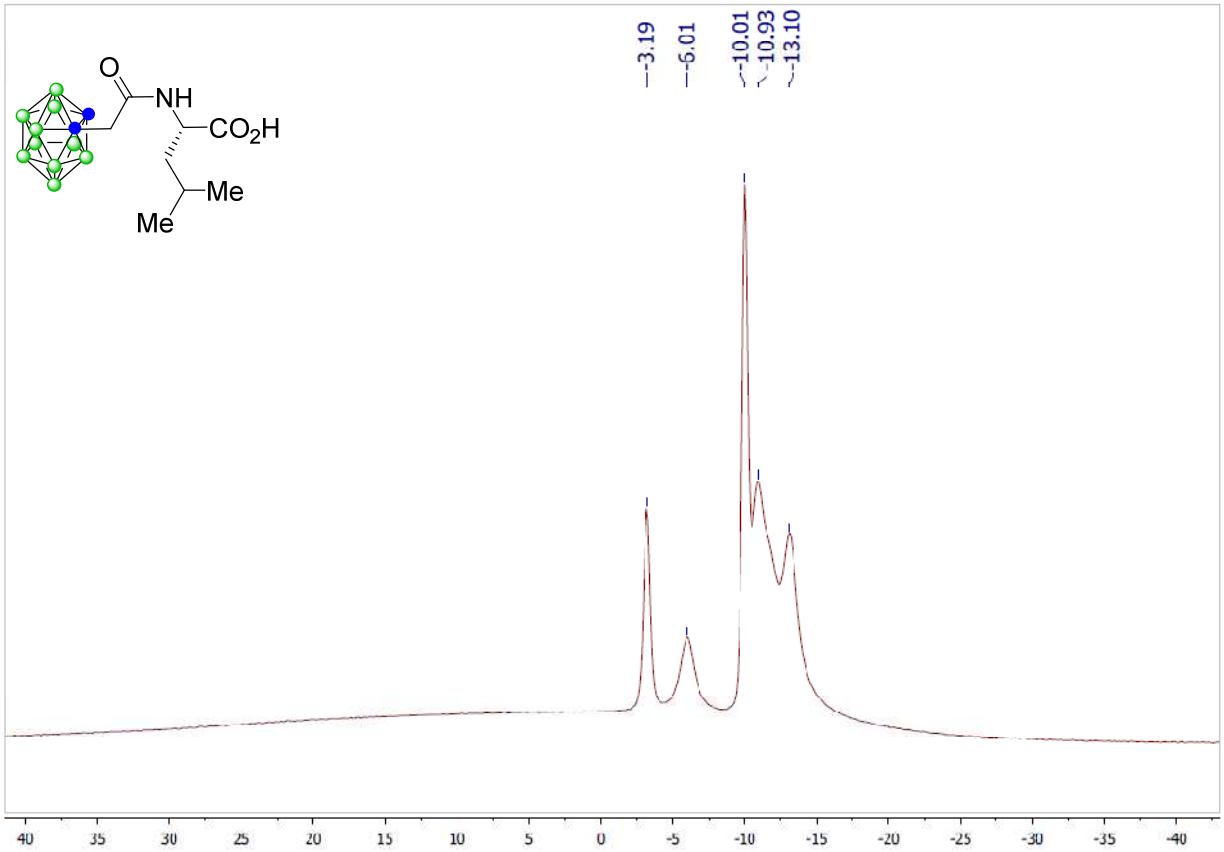

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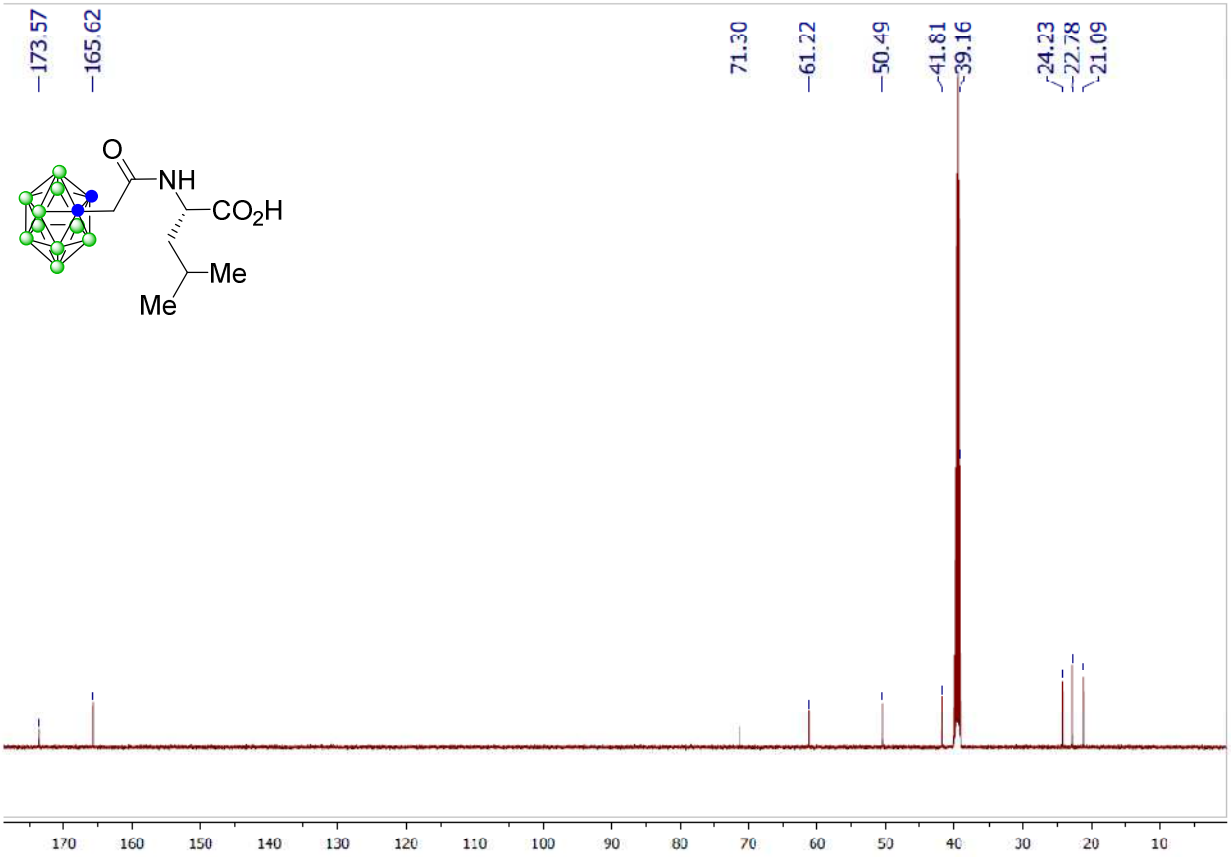

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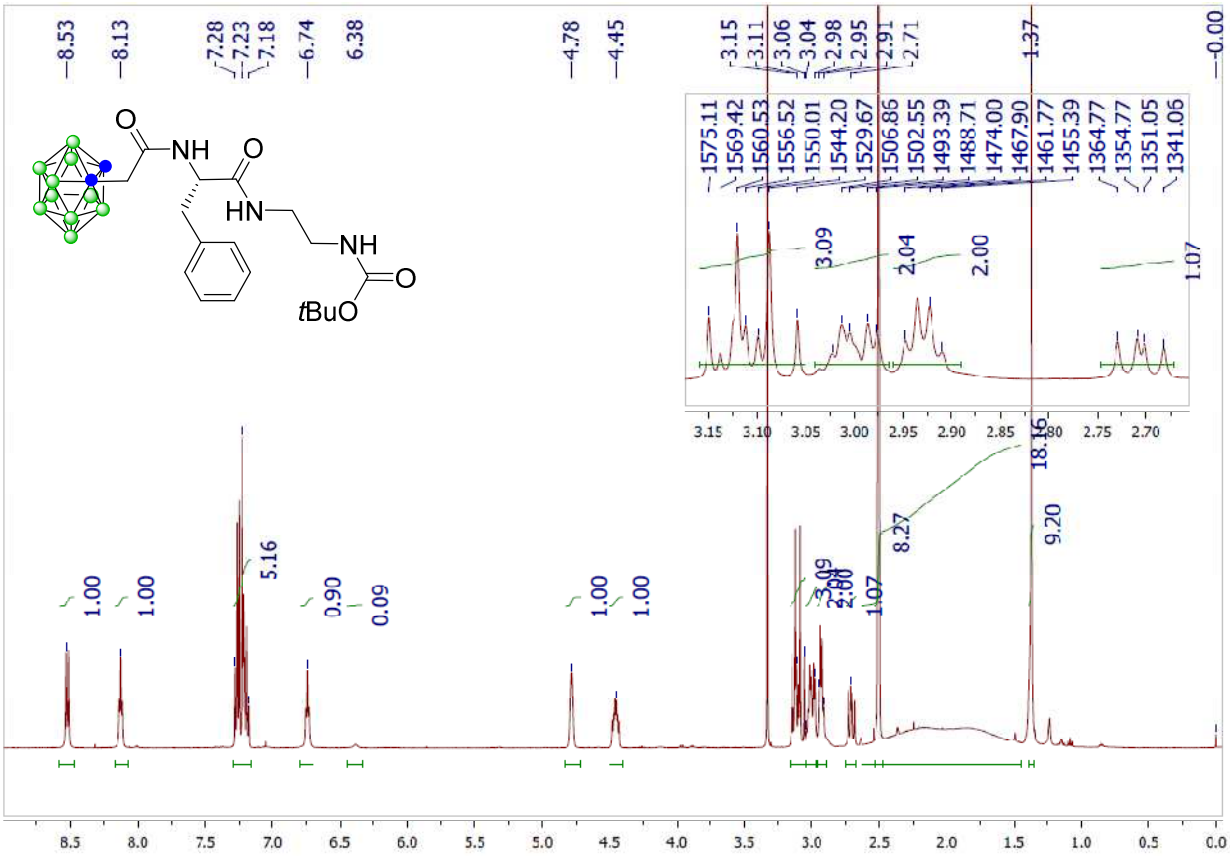

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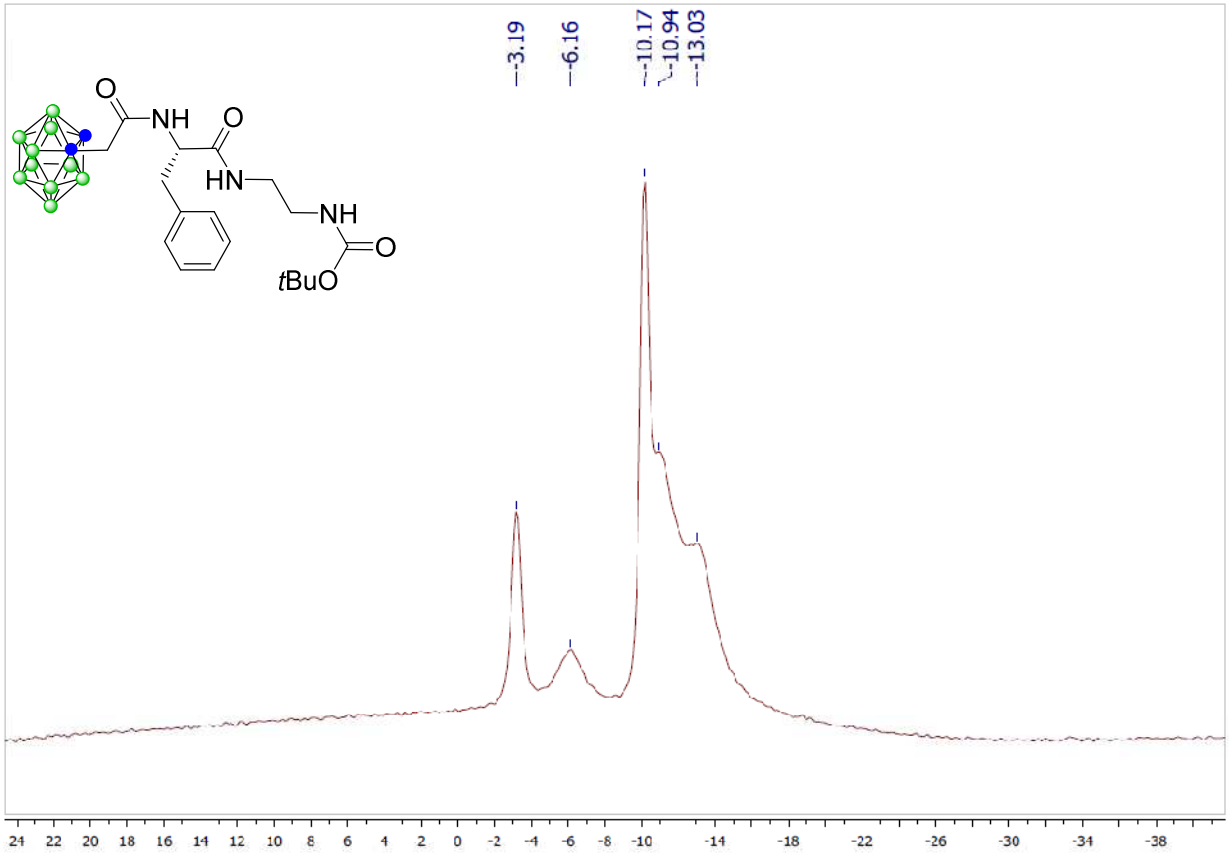
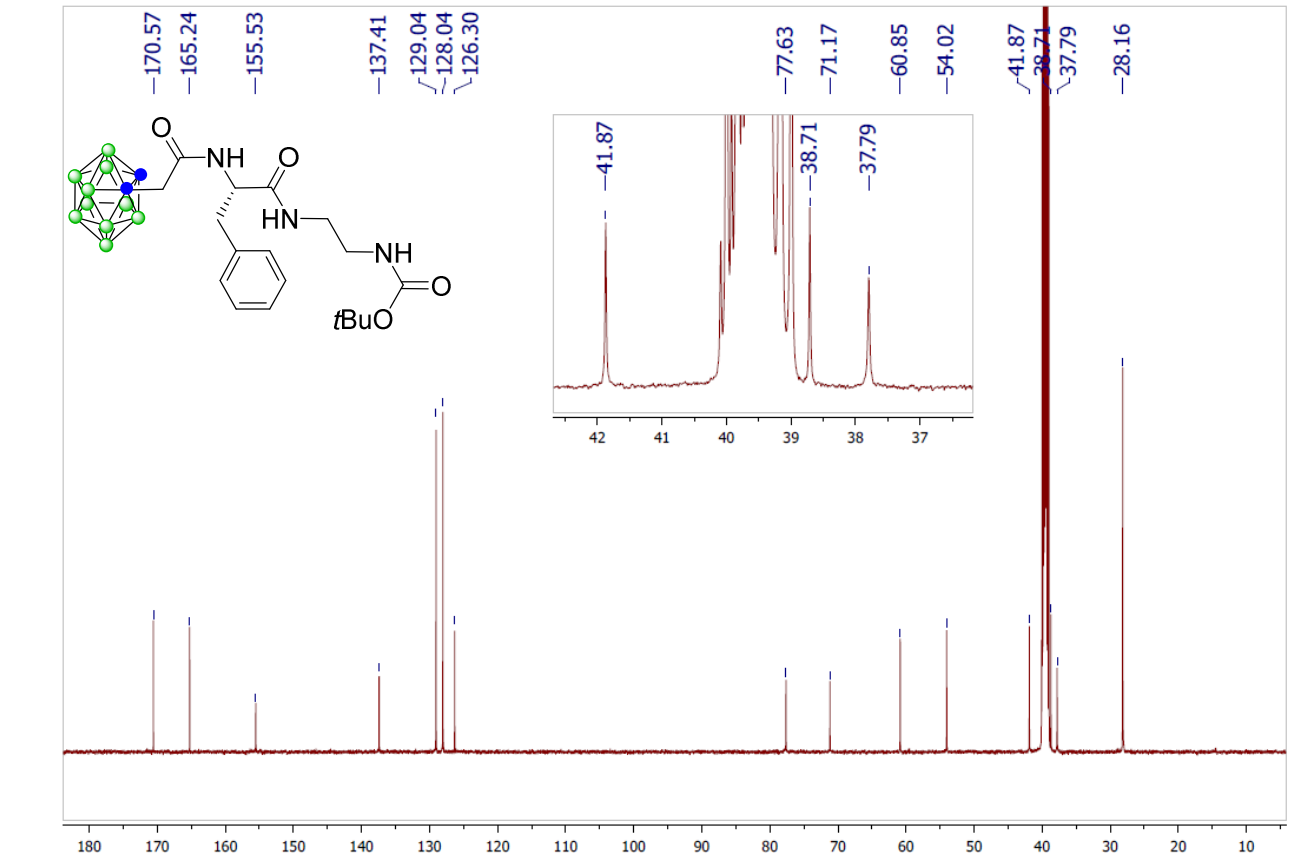


^{11}B{^{1}H} NMR spectrum of compound **5a** (DMSO-d_6, 25 °C, 160 MHz)



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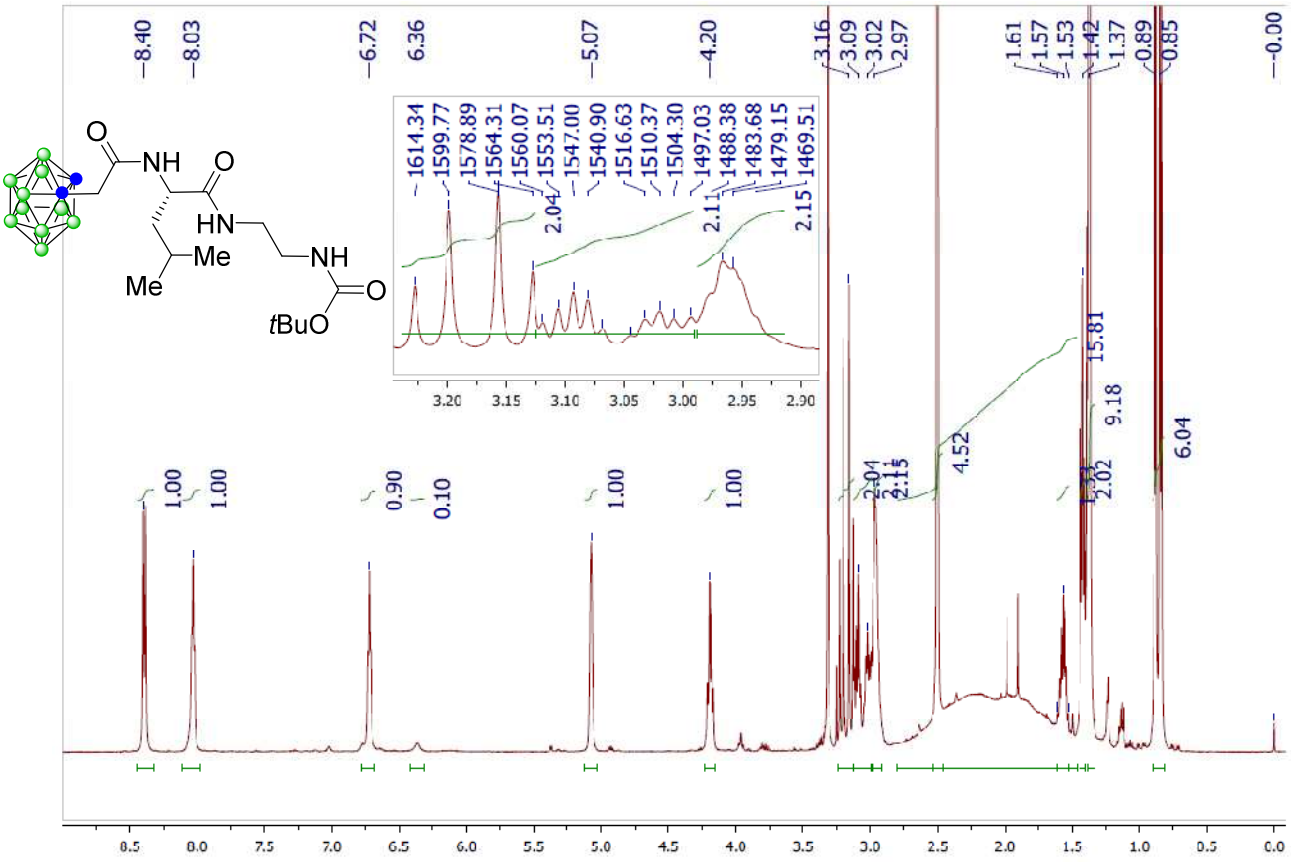

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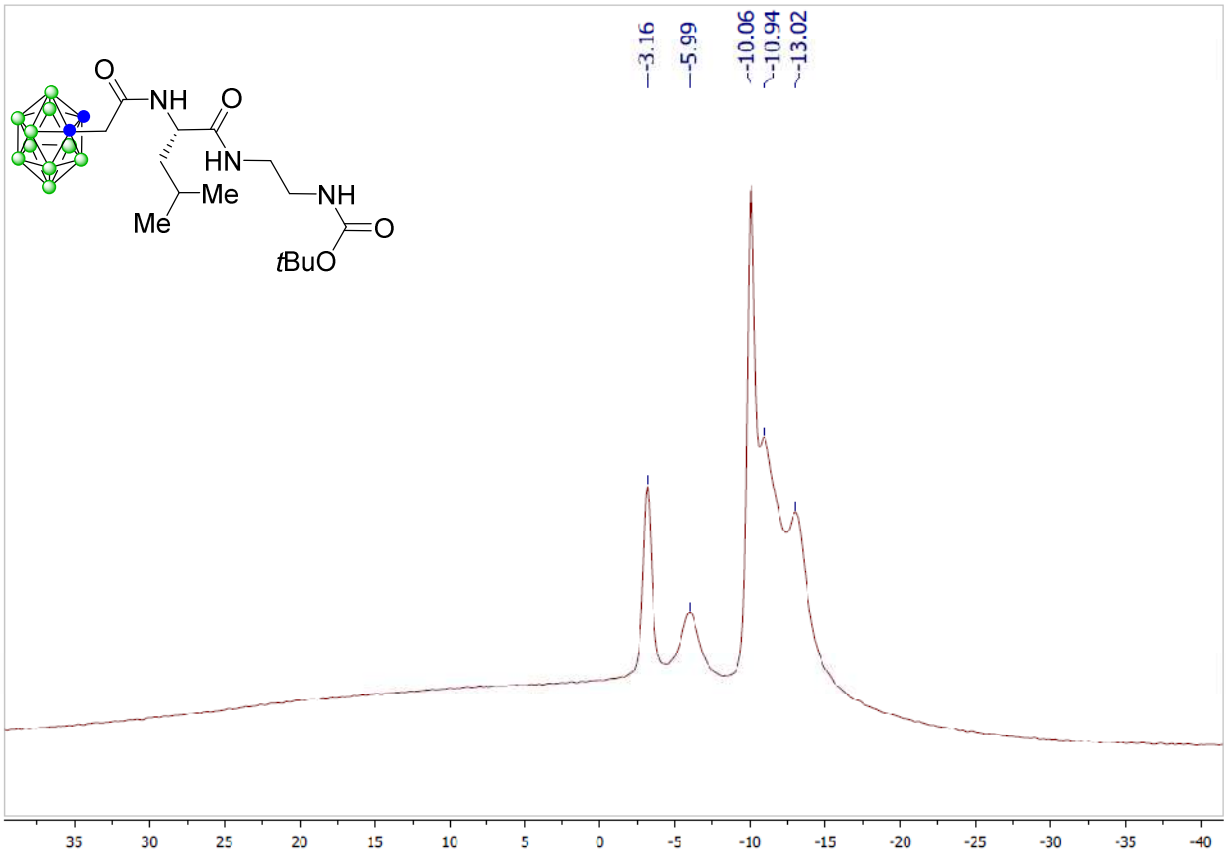

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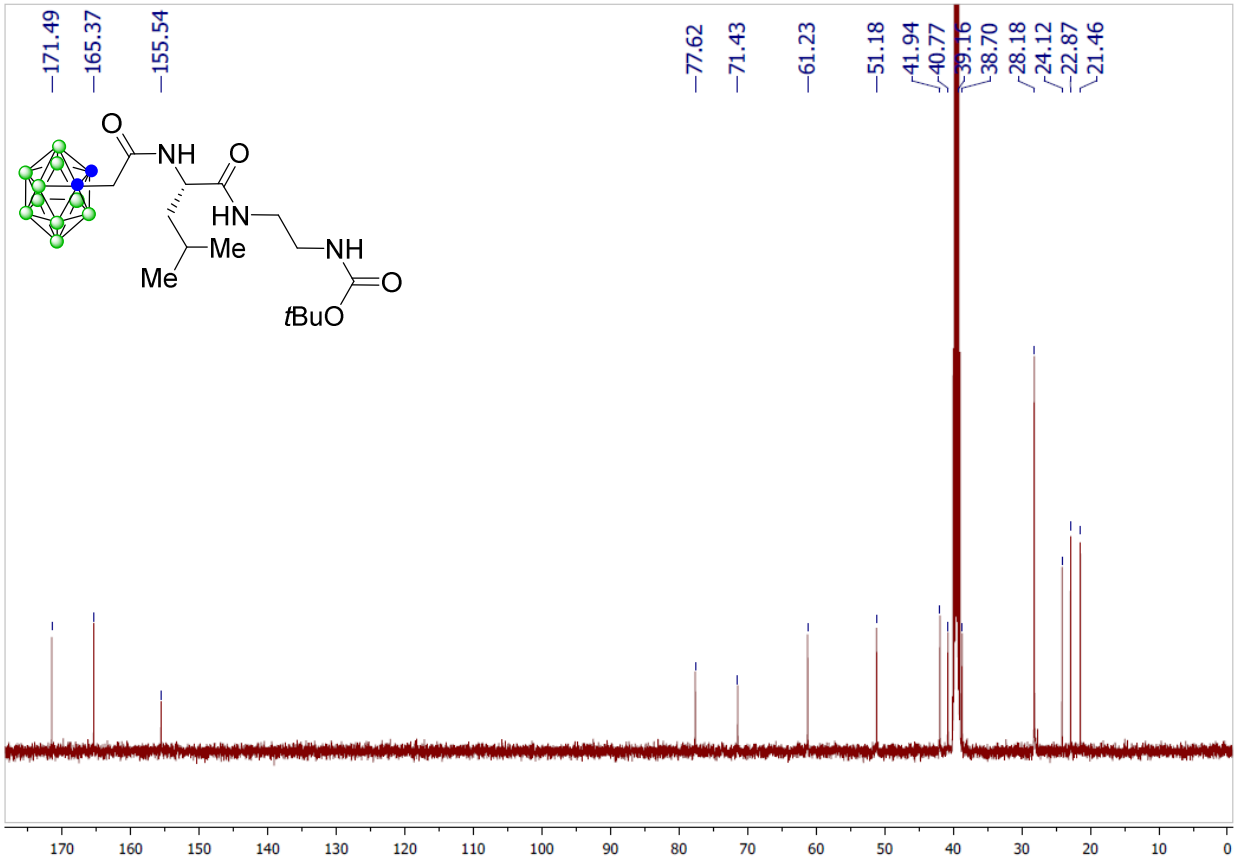

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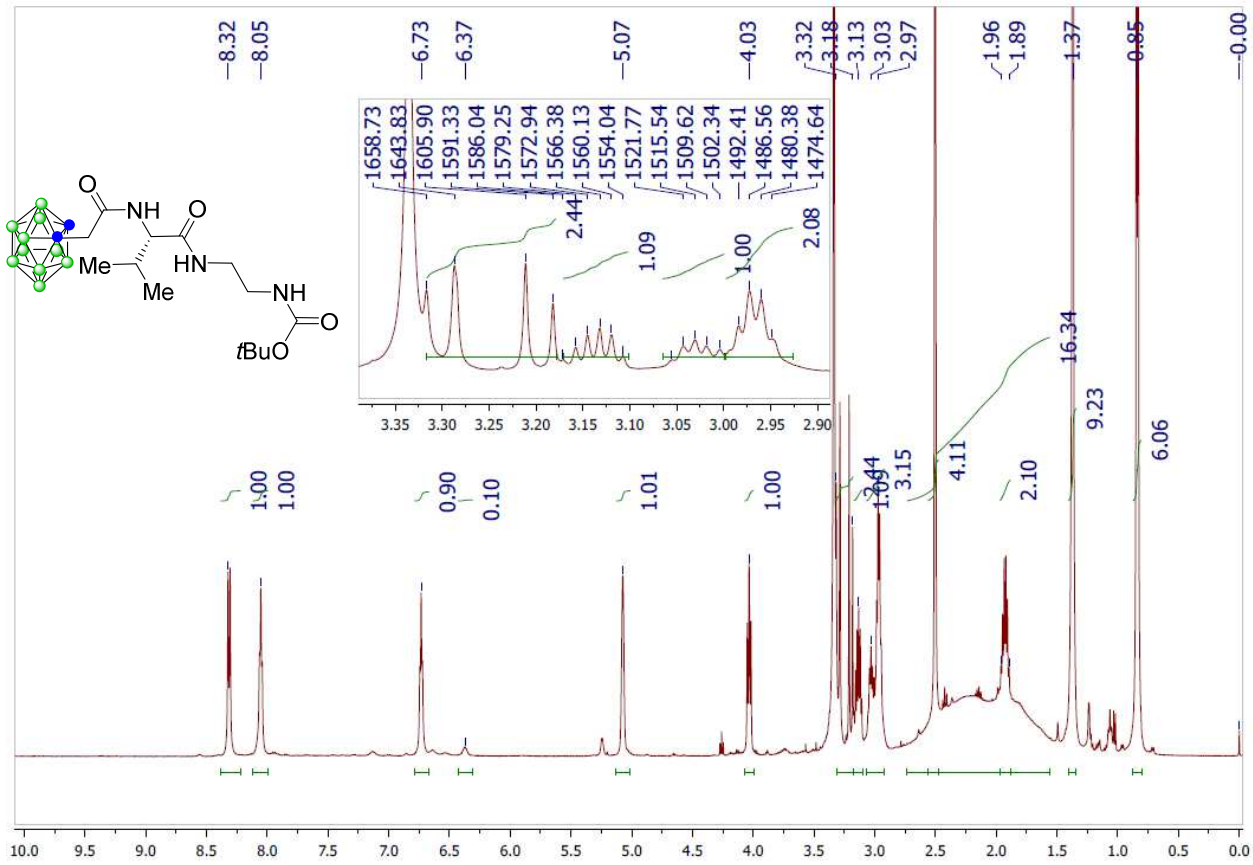
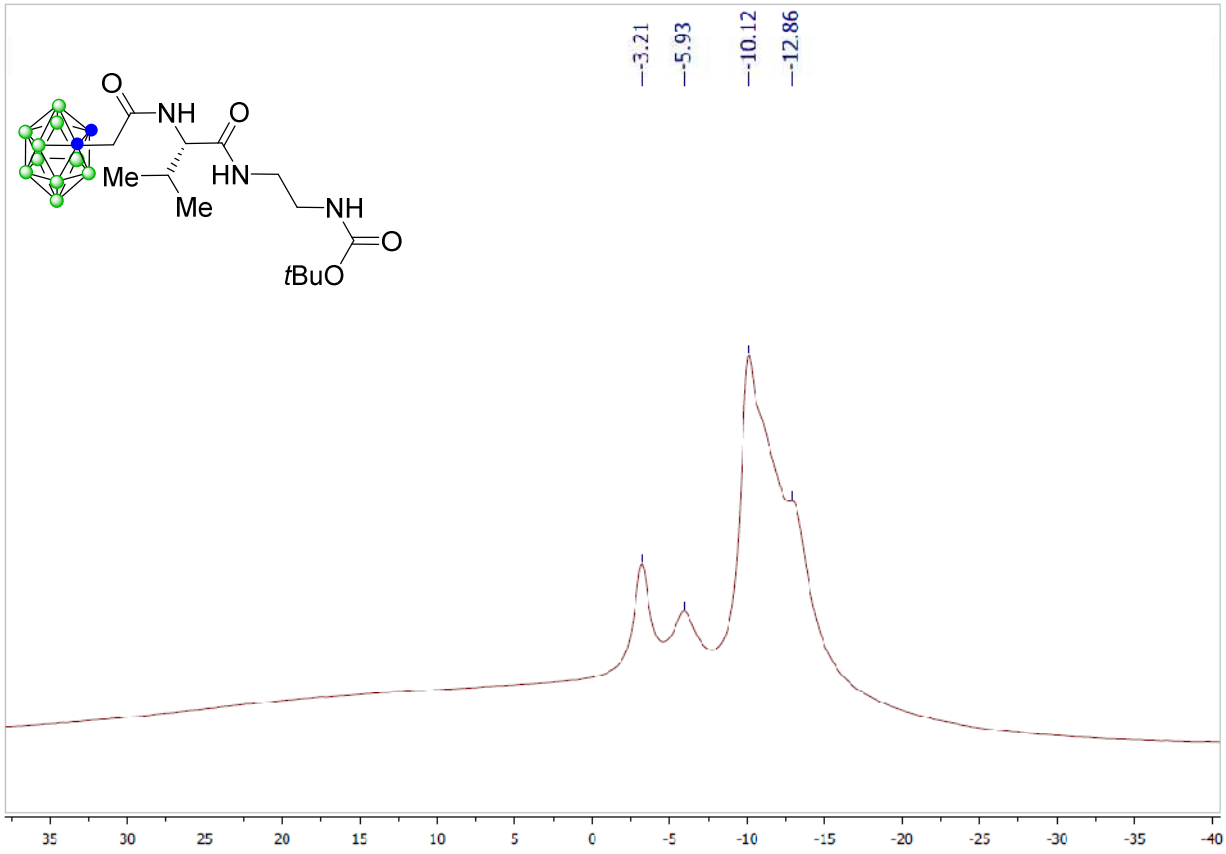
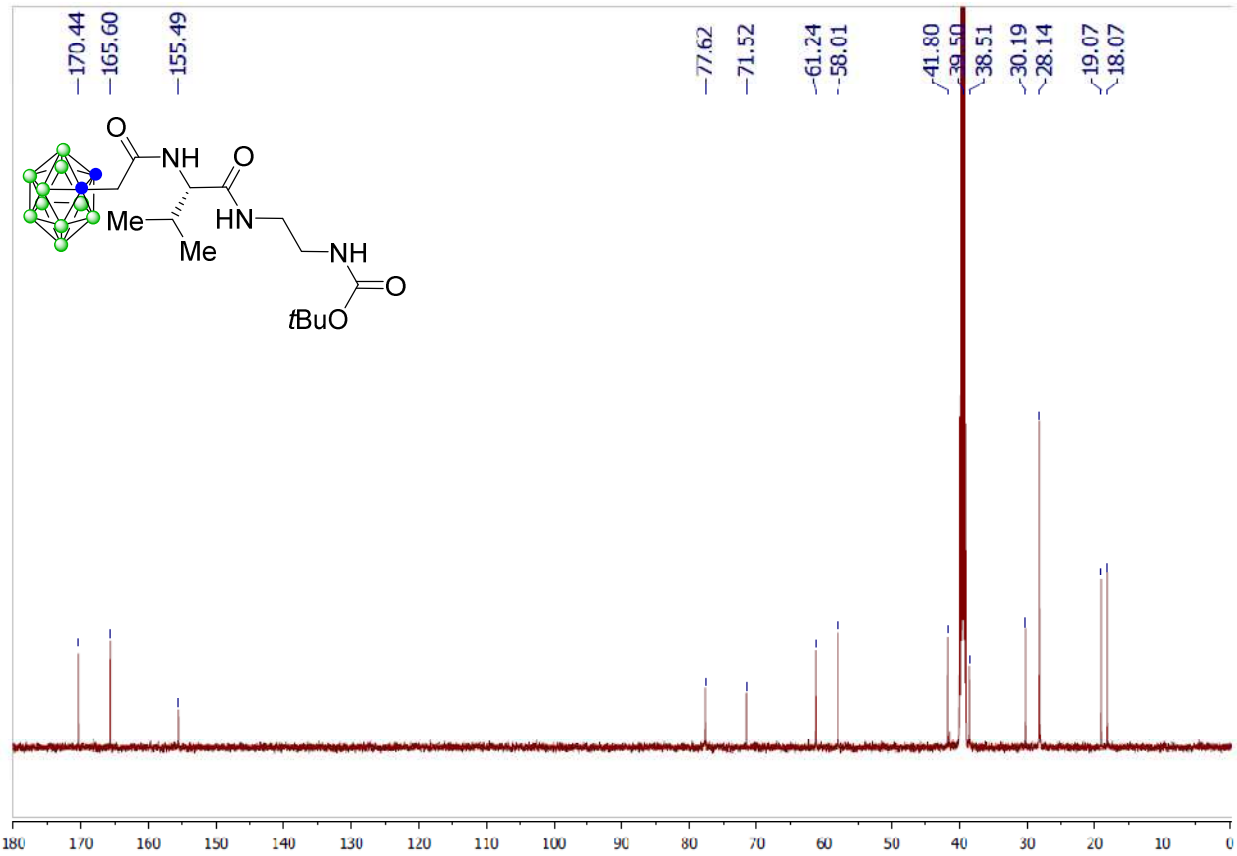


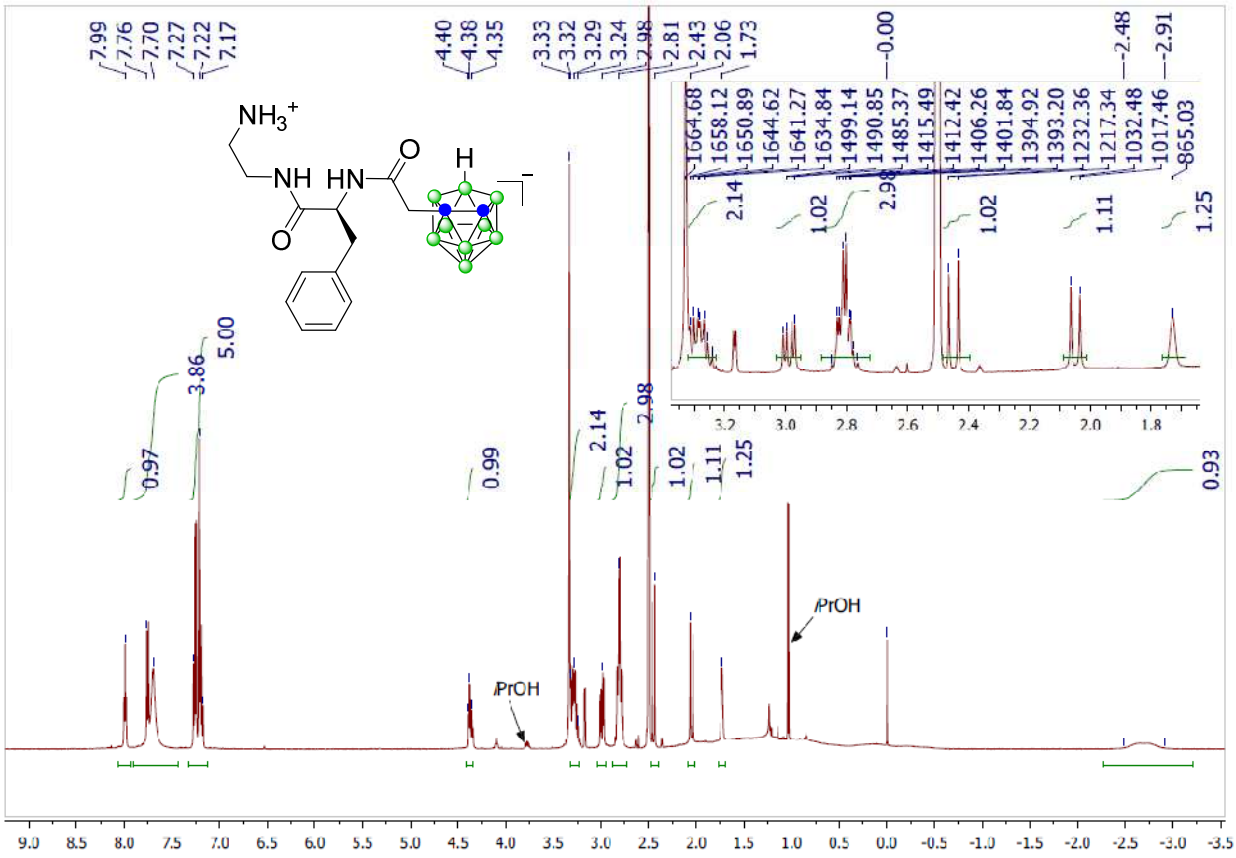
^{1}H NMR spectrum of compound **5c** (DMSO-d_6, 25 °C, 500 MHz)



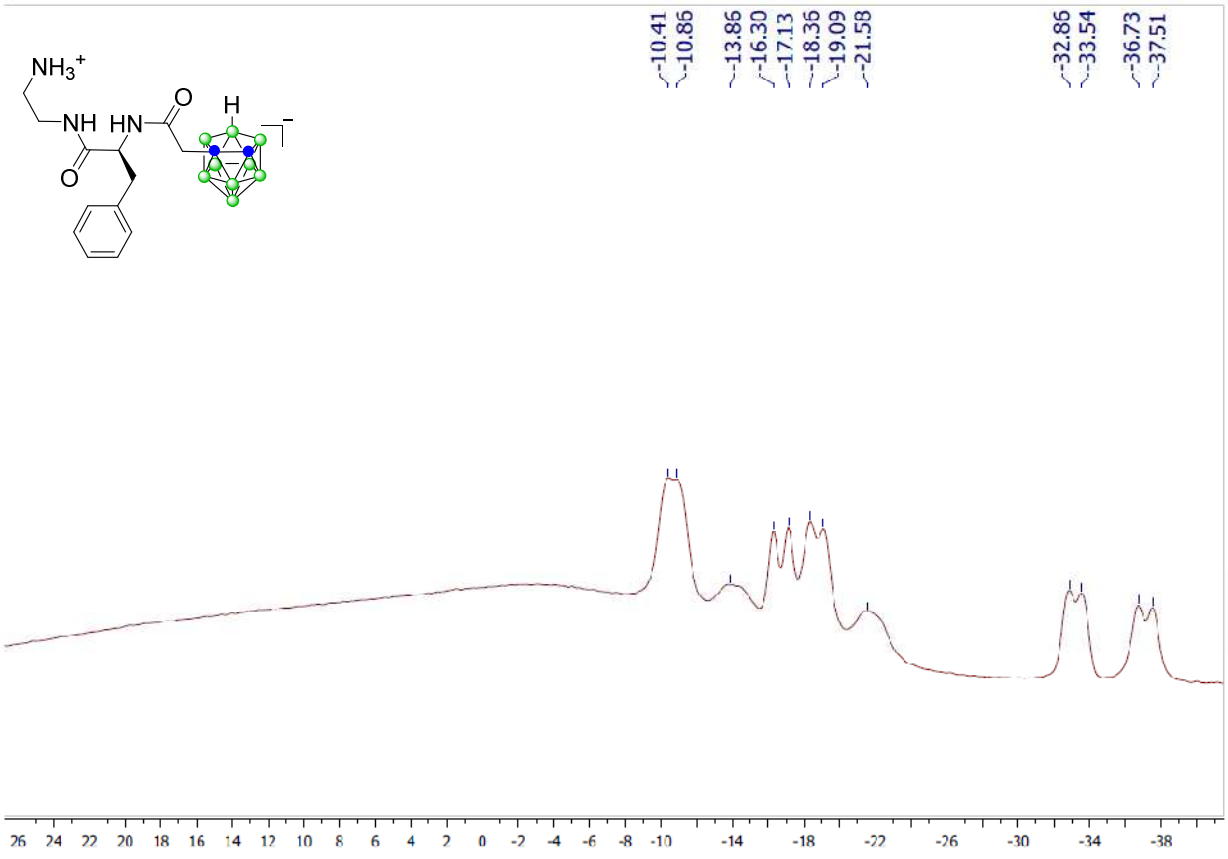
^{11}B{^{1}H} NMR spectrum of compound **5c** (DMSO-d_6, 25 °C, 160 MHz)



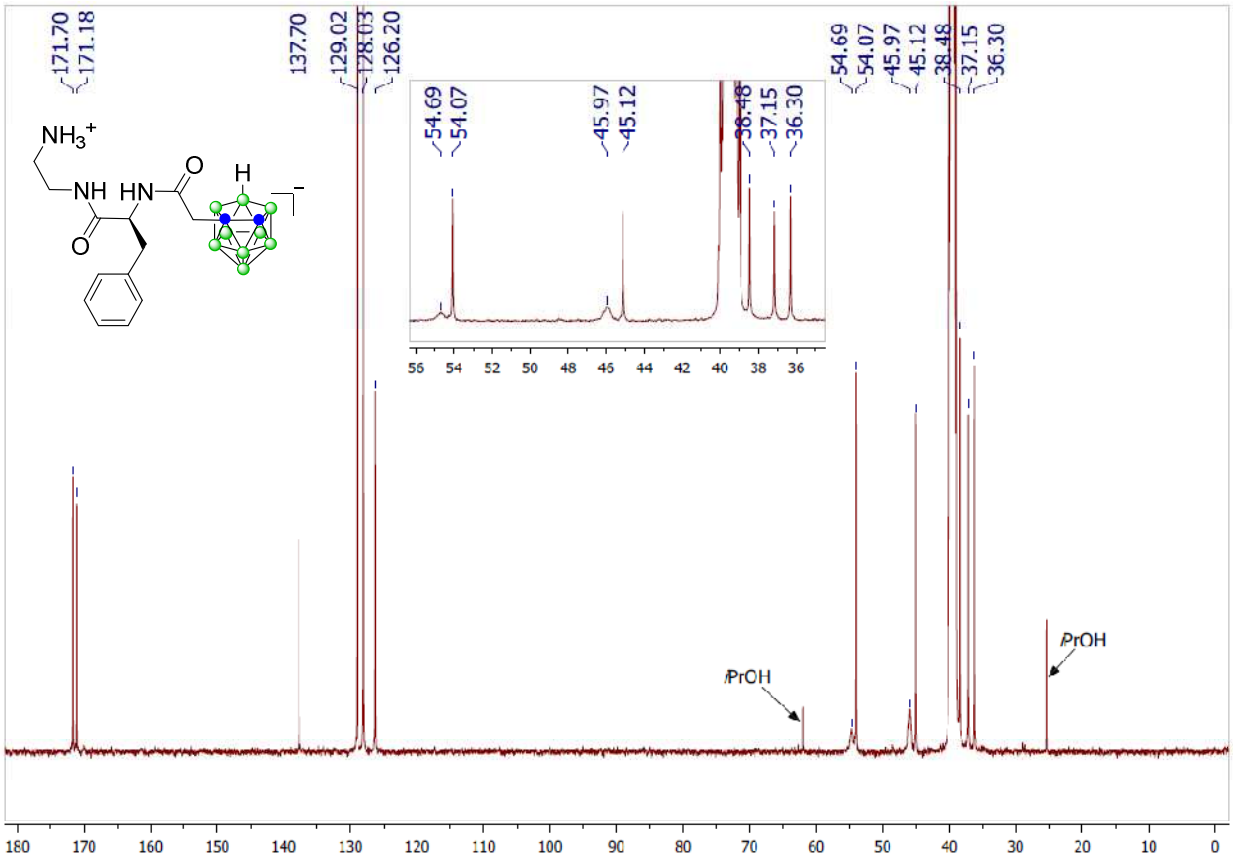
$^{13}C\{^{1}H\}$ NMR spectrum of compound **5c** (DMSO-d_6, 25 °C, 126 MHz)



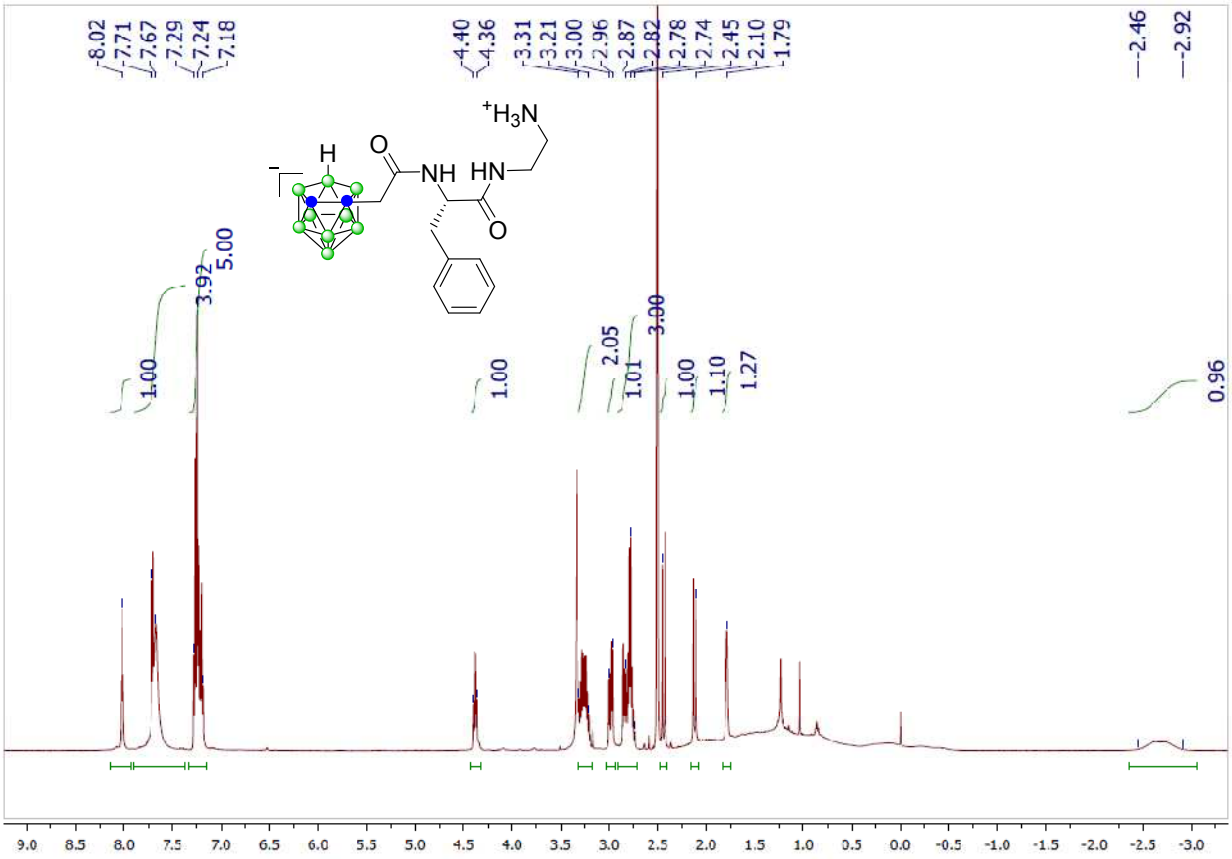
^{1}H NMR spectrum of compound (S,R_P)-**7a** (DMSO-d_6, 25 °C, 500 MHz)



Proton-coupled ^{11}B NMR spectrum of compound (*S*,*R*$_P$)-**7a** (DMSO-*d*$_6$, 25 °C, 160 MHz)



^{13}C{^{1}H} NMR spectrum of compound (*S*,*R*$_P$)-**7a** (DMSO-*d*$_6$, 25 °C, 126 MHz)



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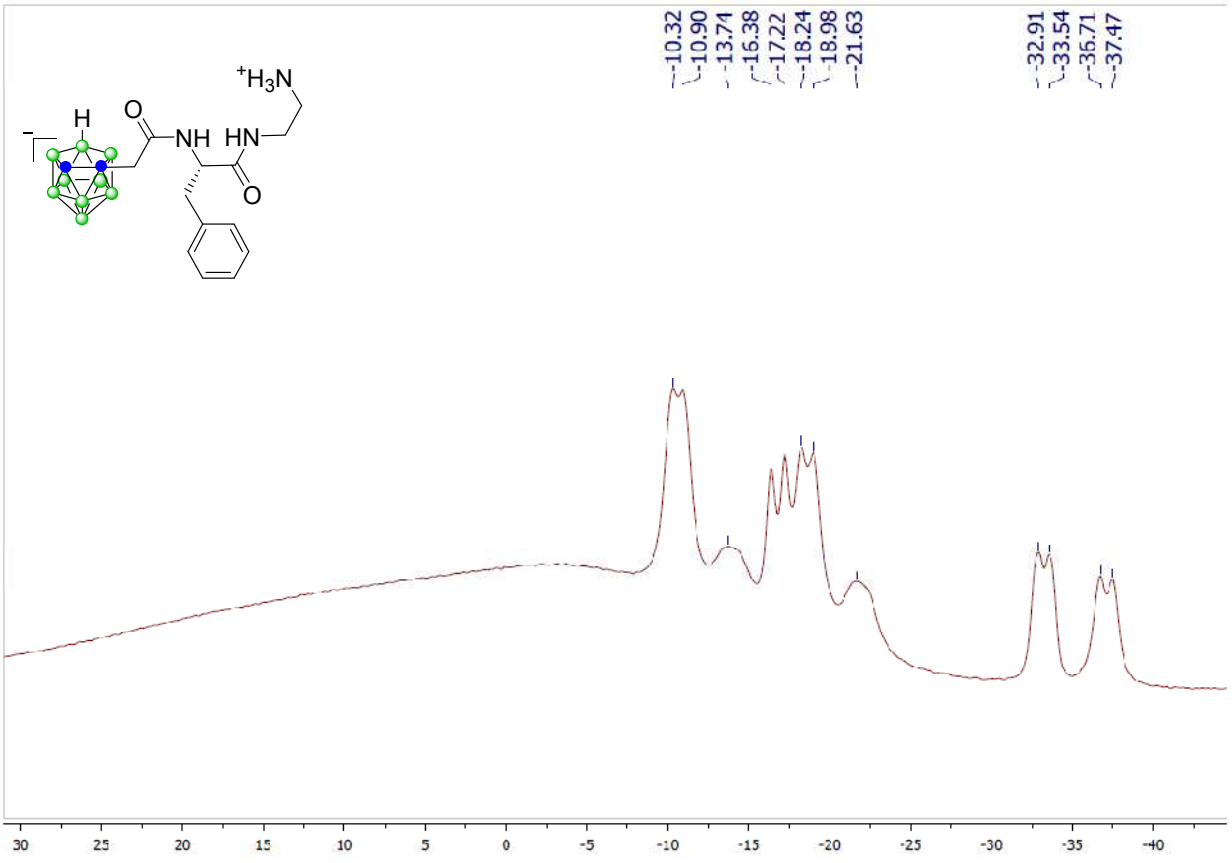
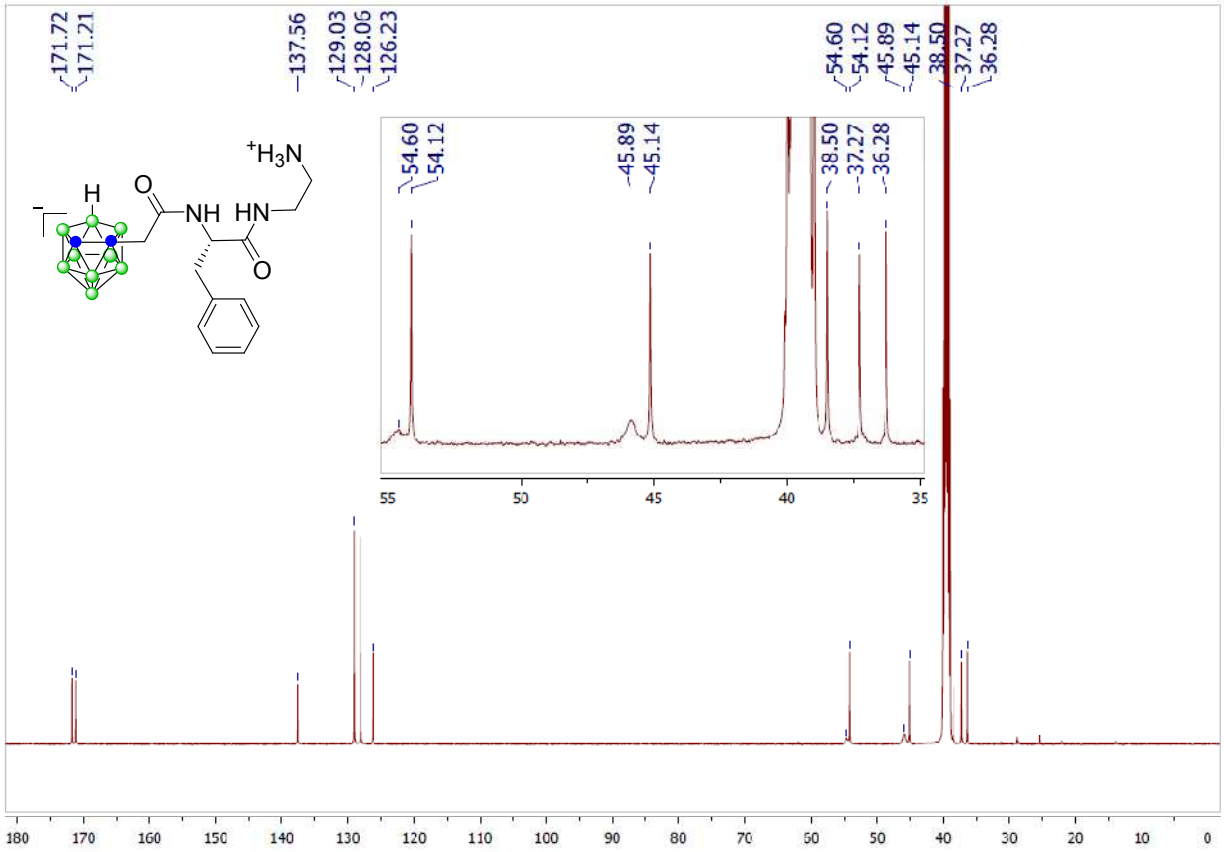
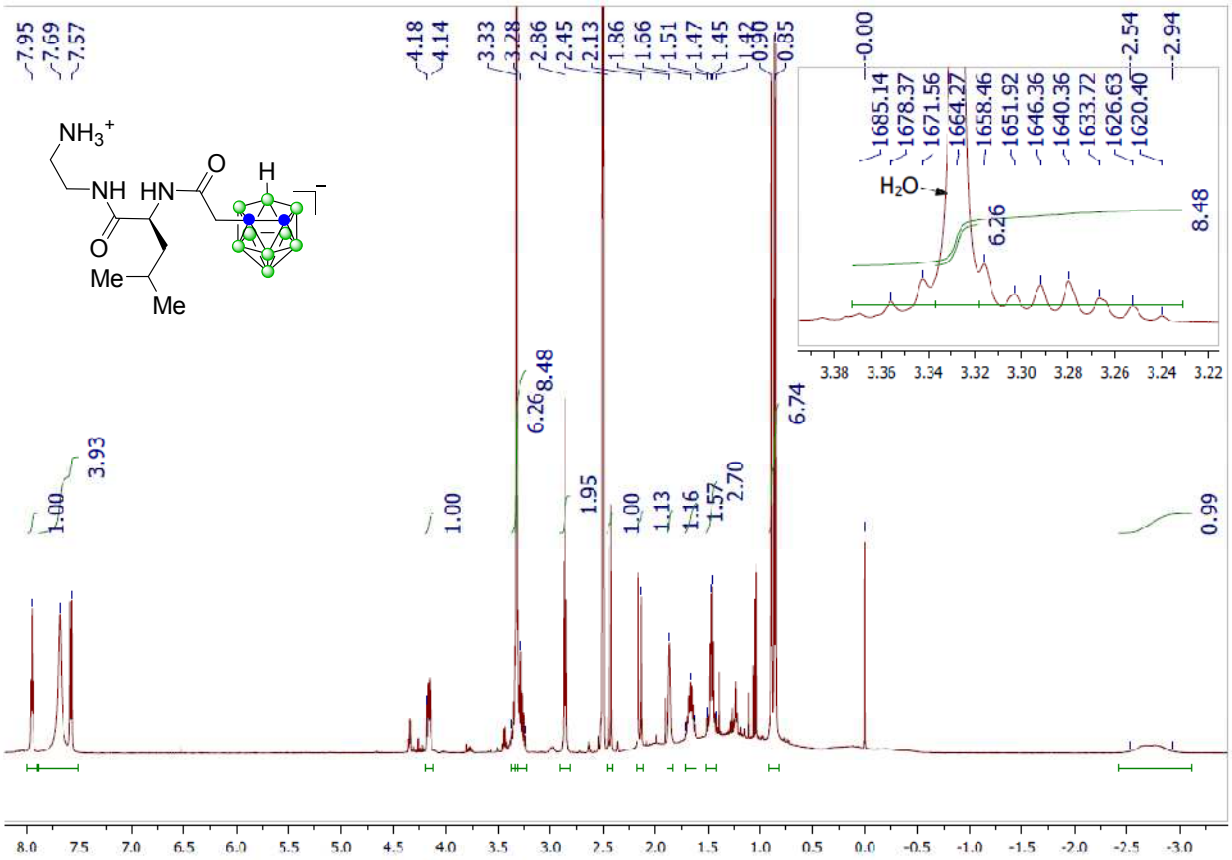


Proton-coupled ^{11}B NMR spectrum of compound (S,S_P)-**7a** (DMSO-d_6, 25 °C, 160 MHz)



$^{13}C\{^{1}H\}$ NMR spectrum of compound (S,S_P)-**7a** (DMSO-d_6, 25 °C, 126 MHz)



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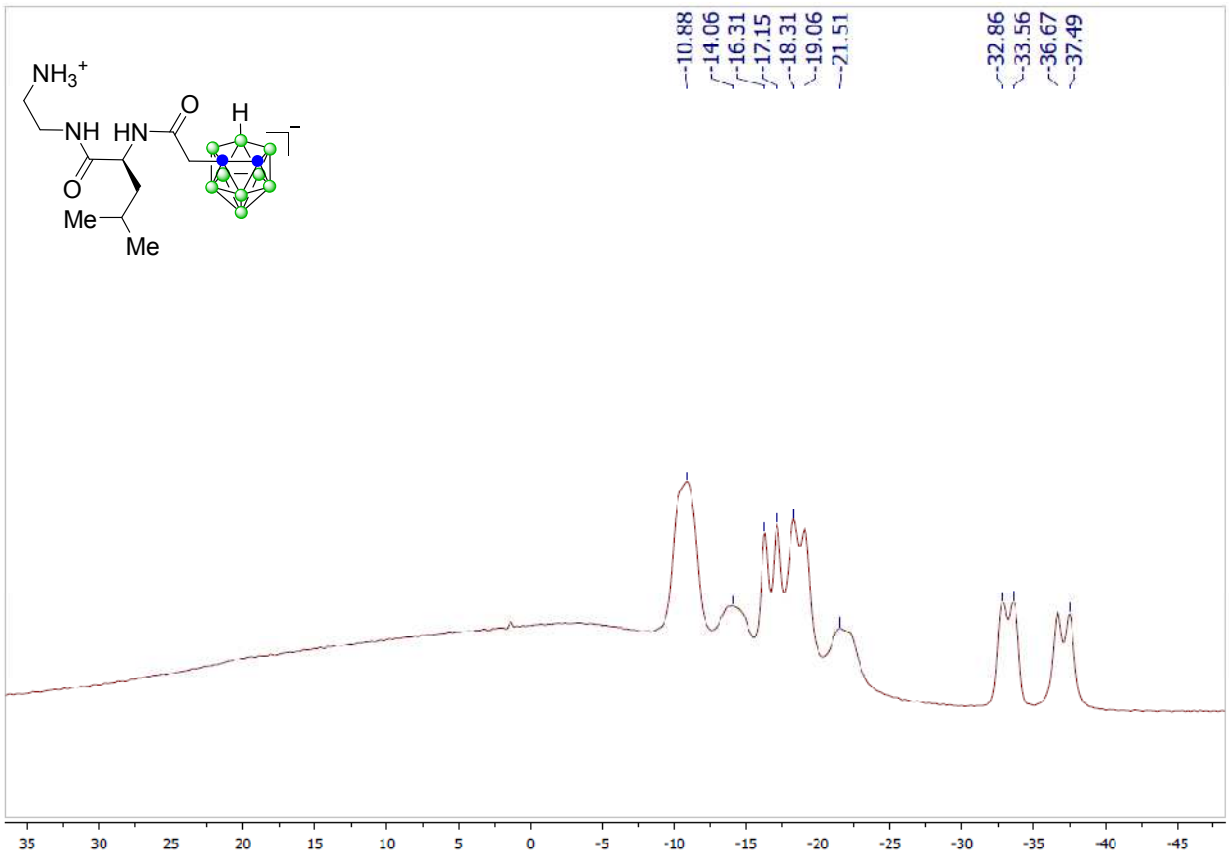
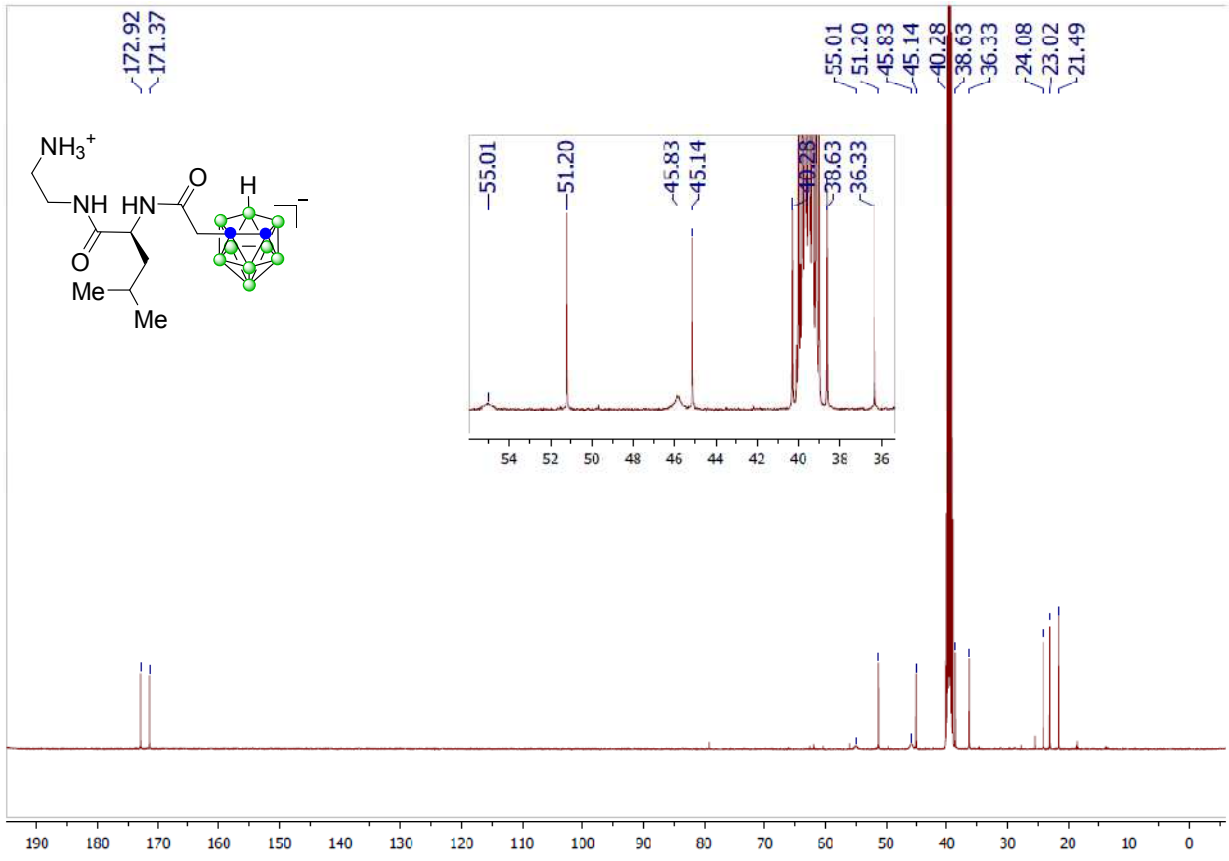
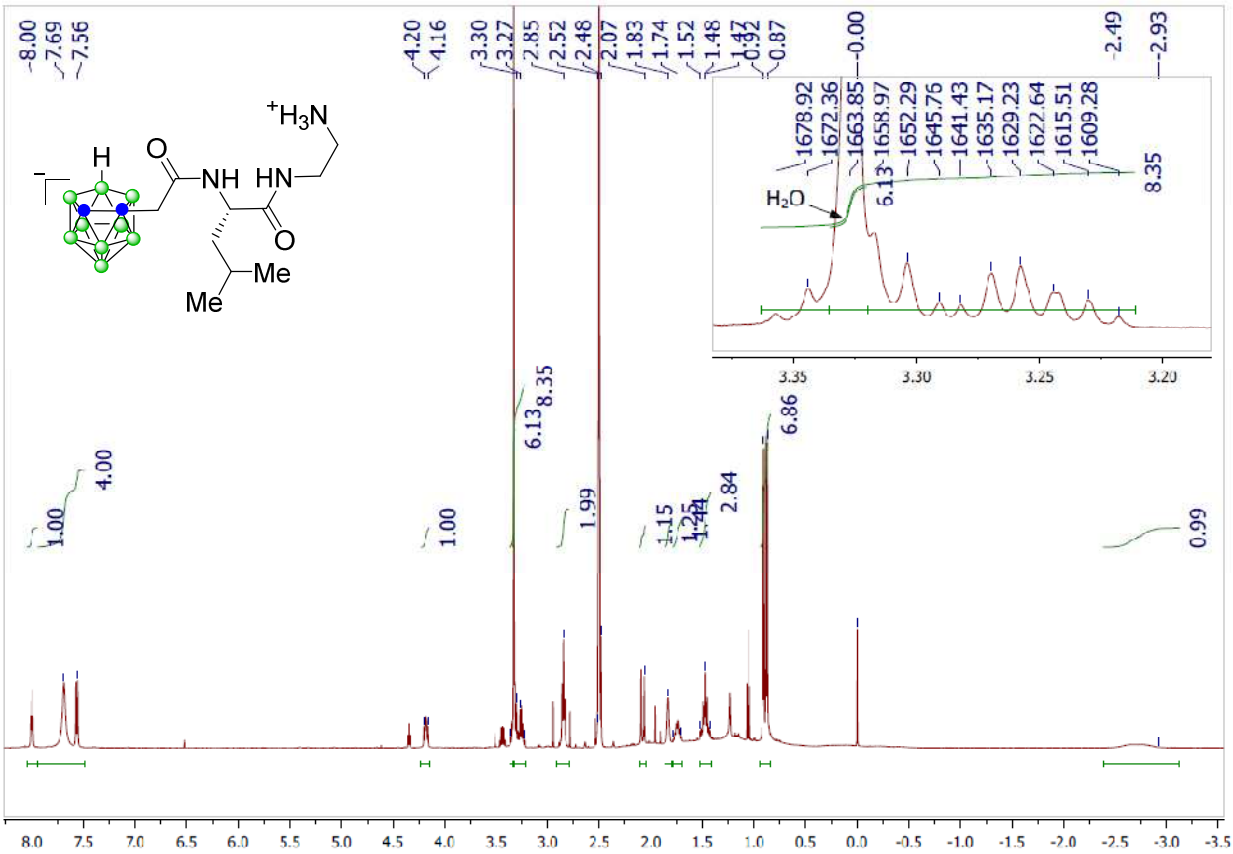


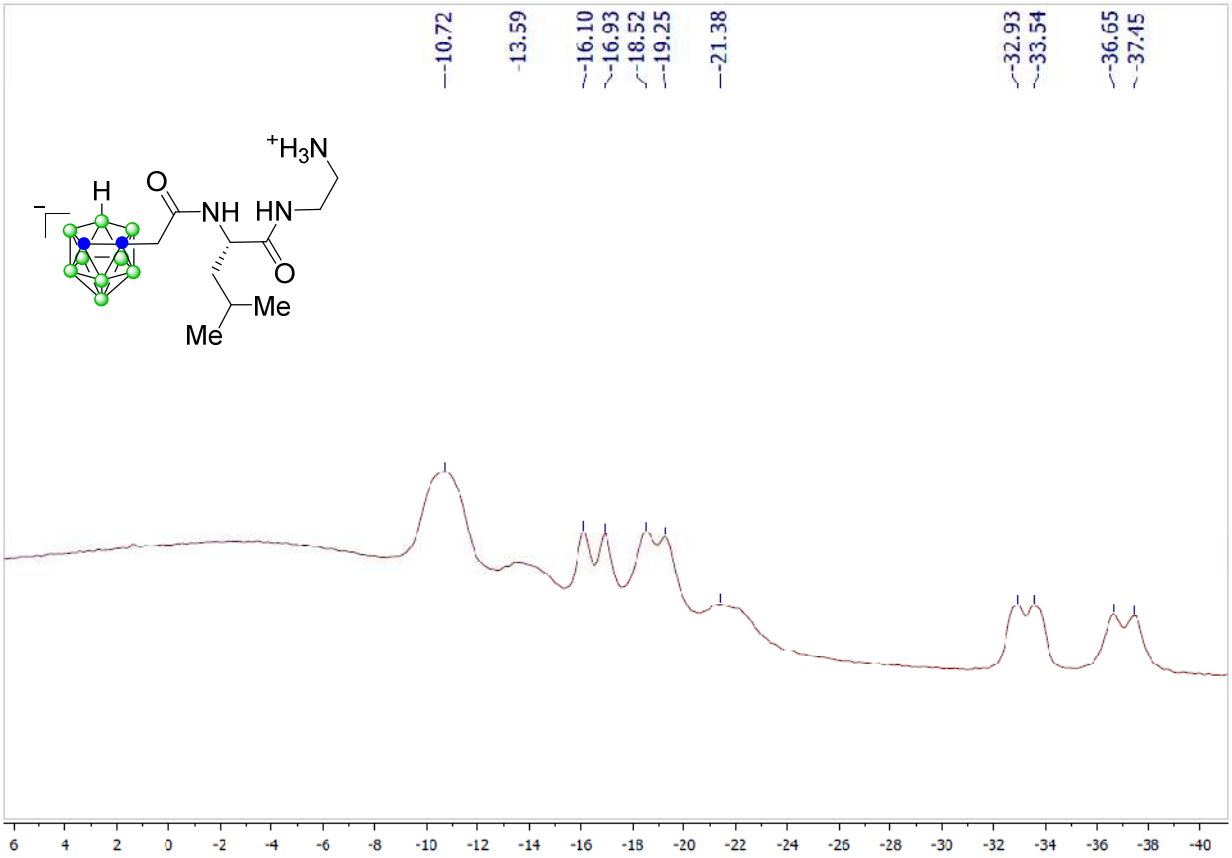
Proton-coupled ^{11}B NMR spectrum of compound (*S*,*R*$_P$)-**7b** (DMSO-*d*$_6$, 25 °C, 160 MHz)



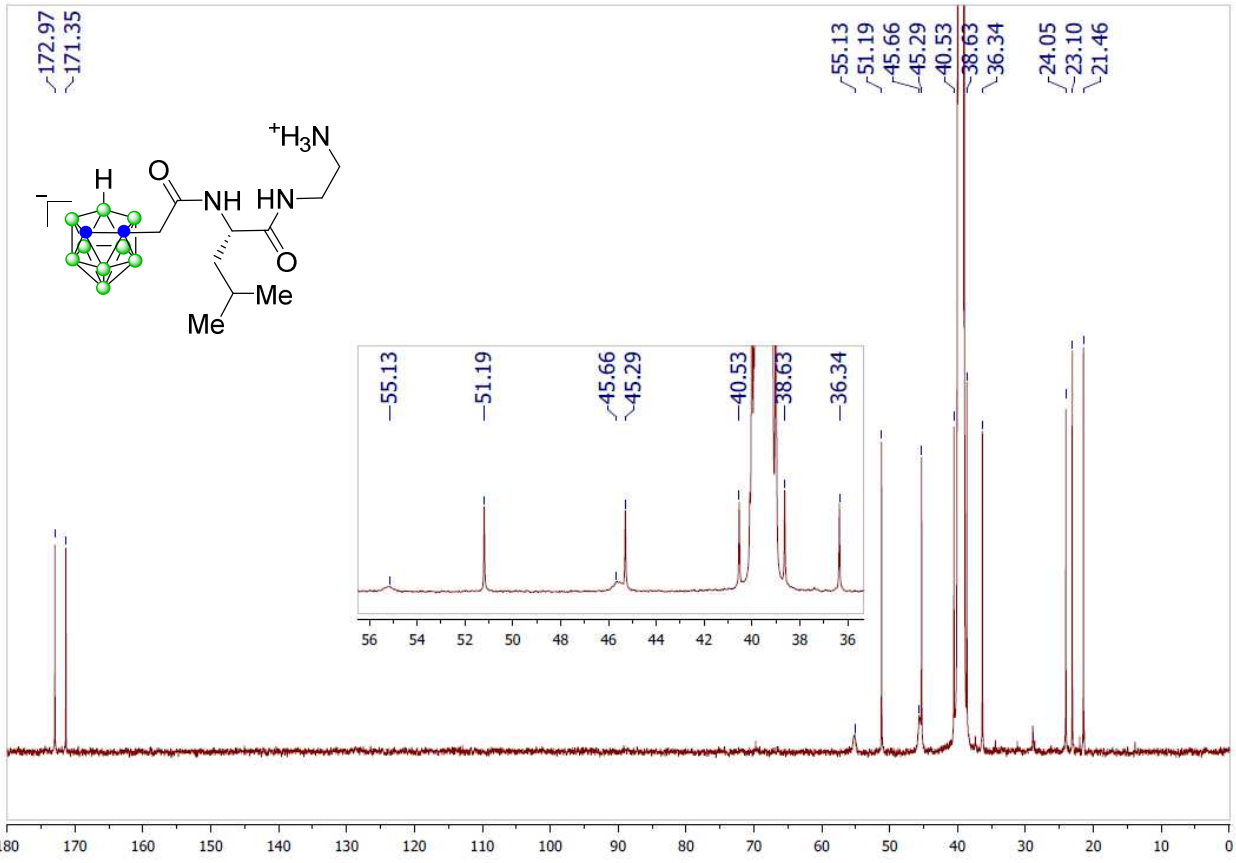
^{13}C{^{1}H} NMR spectrum of compound (*S*,*R*$_P$)-**7b** (DMSO-*d*$_6$, 25 °C, 126 MHz)



^{1}H NMR spectrum of compound (S,S_P)-**7b** (DMSO-d_6, 25 °C, 500 MHz)



Proton-coupled ^{11}B NMR spectrum of compound (S,S_P)-**7b** (DMSO-d_6, 25 °C, 160 MHz)



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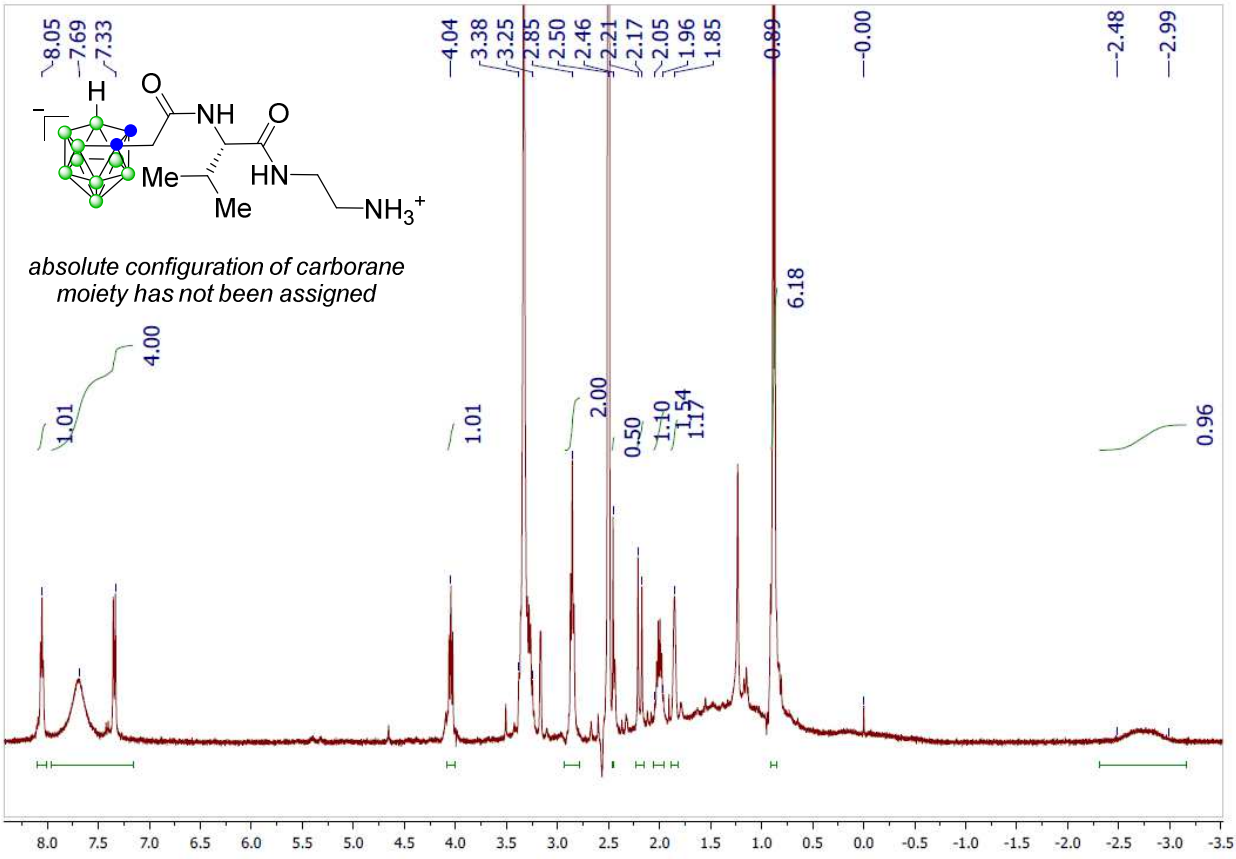

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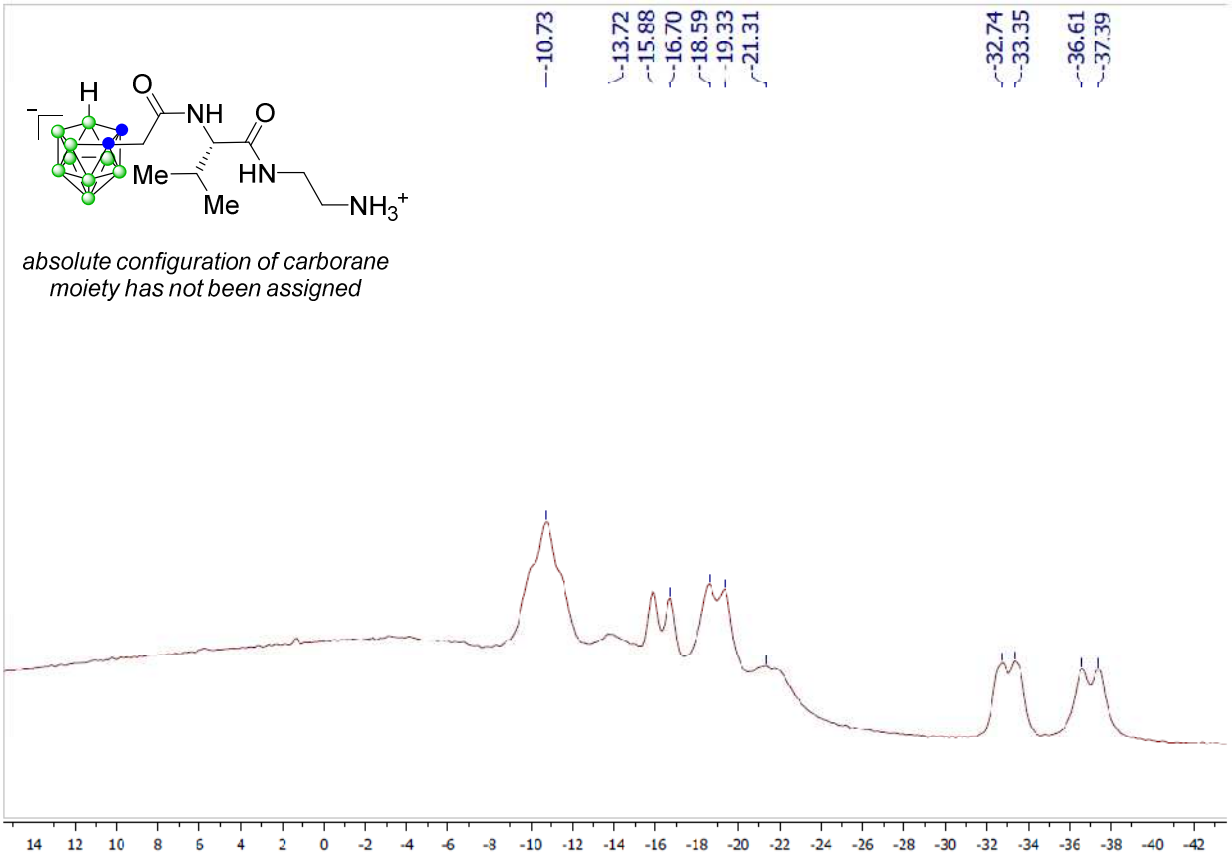
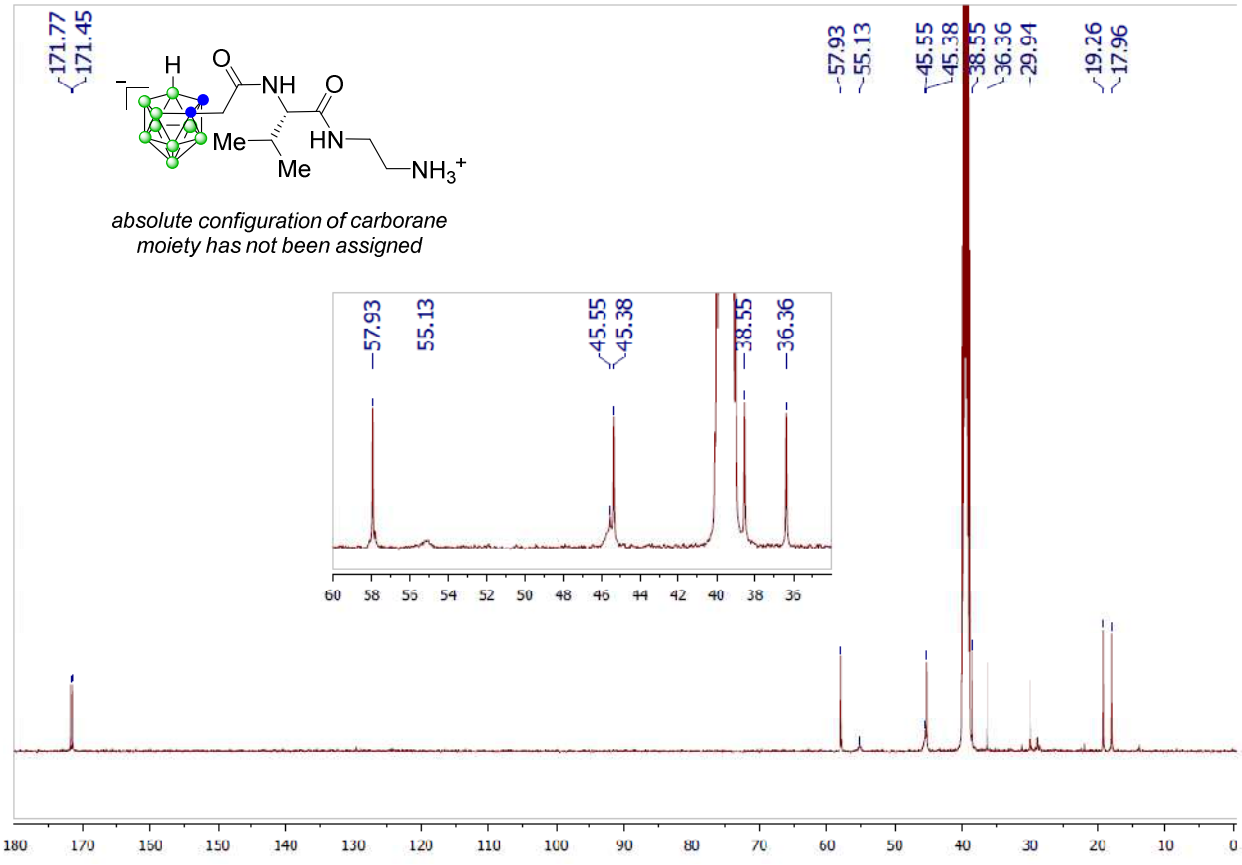
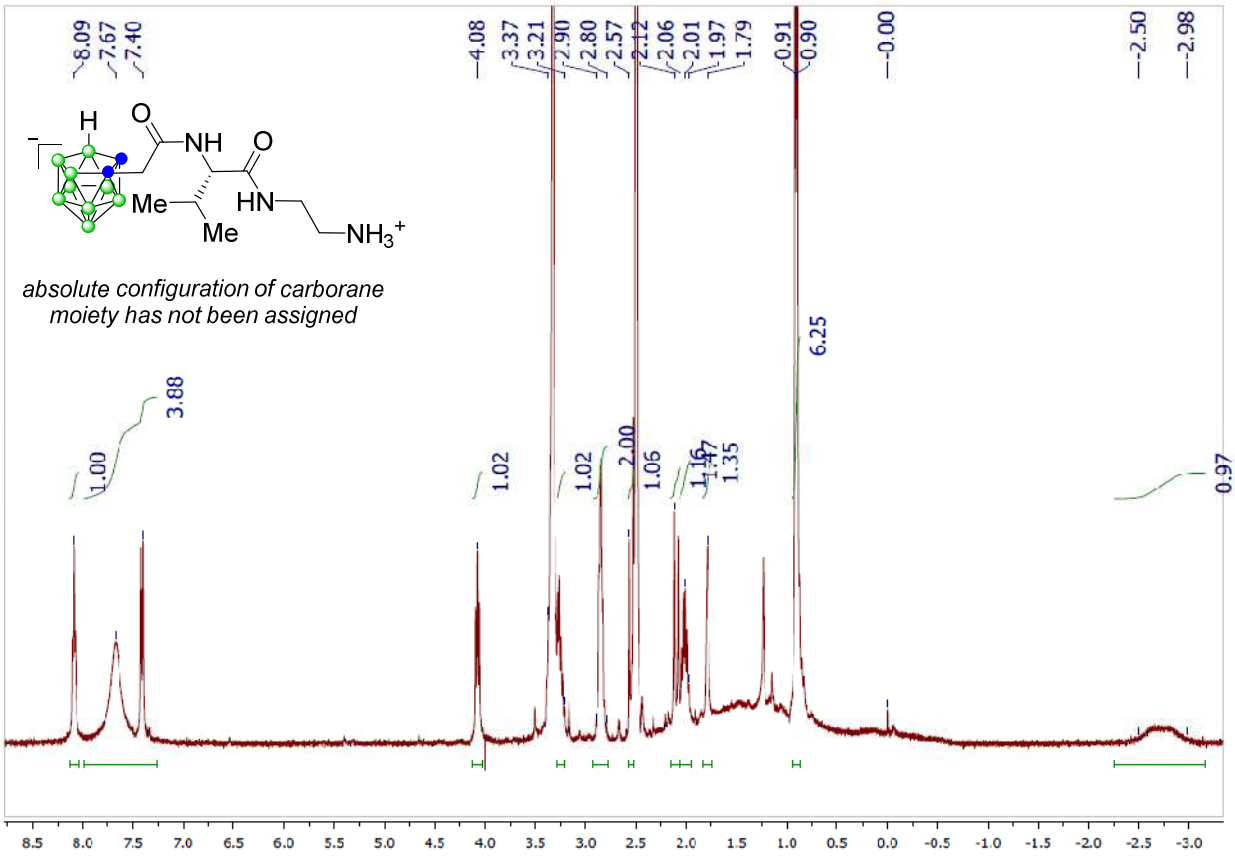


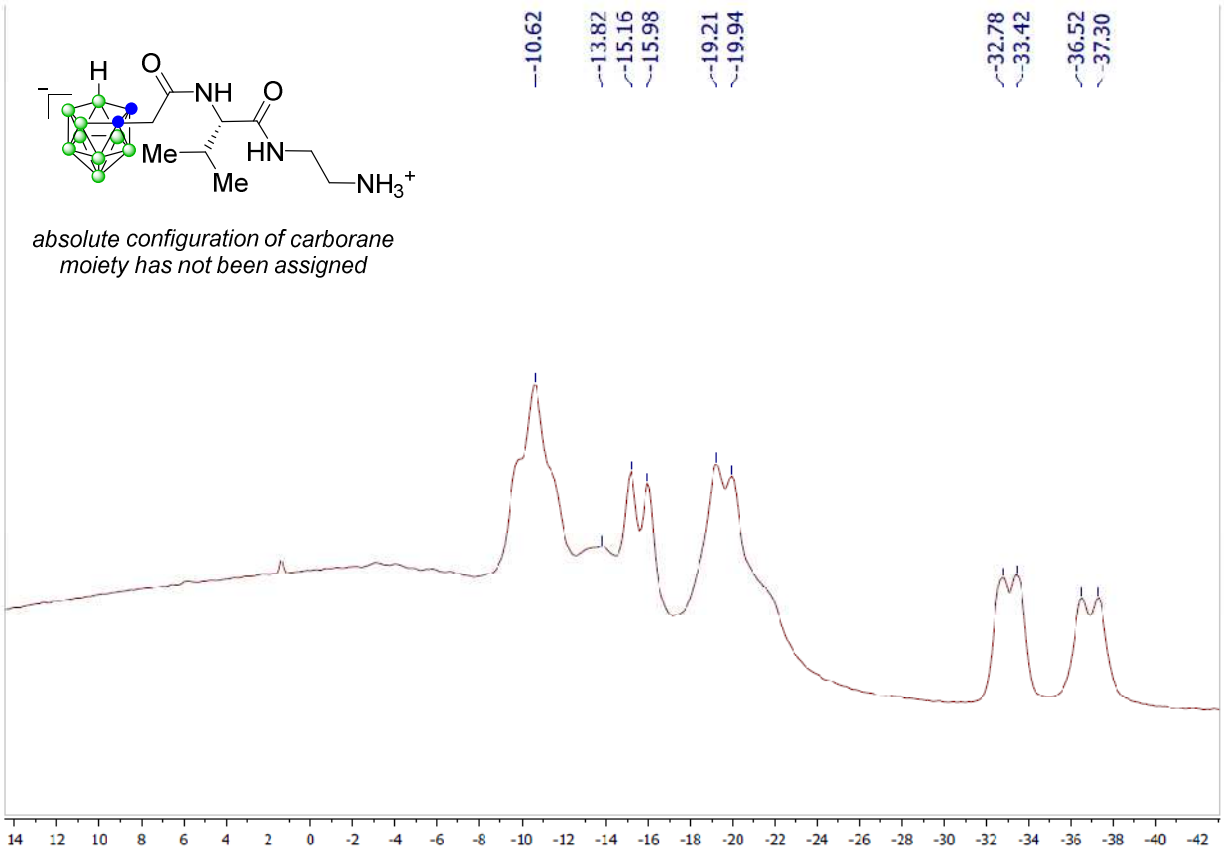
Proton-coupled ^{11}B NMR spectrum of compound **7c** (***diastereomer I***) (DMSO-d_6, 25 °C, 160 MHz)



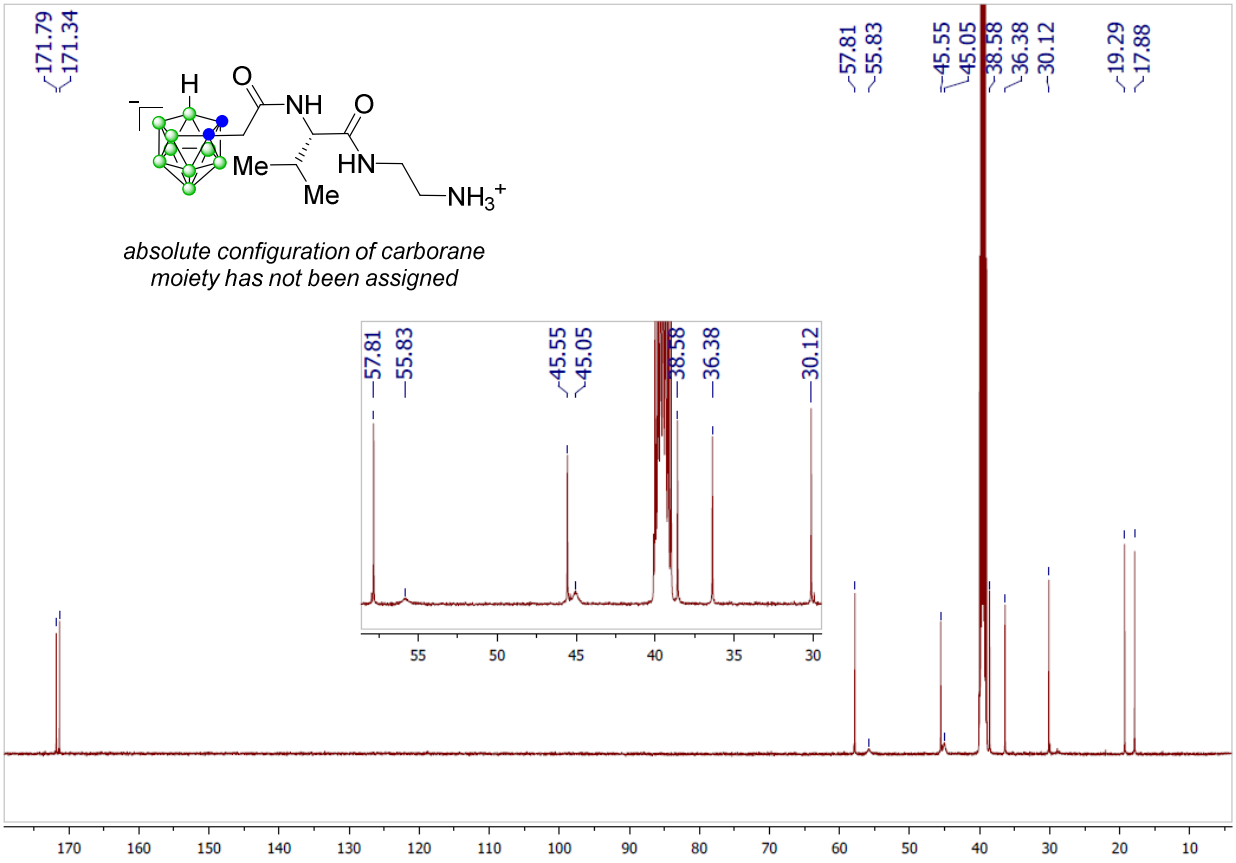
^{13}C{^{1}H} NMR spectrum of compound **7c** (***diastereomer I***) (DMSO-d_6, 25 °C, 126 MHz)



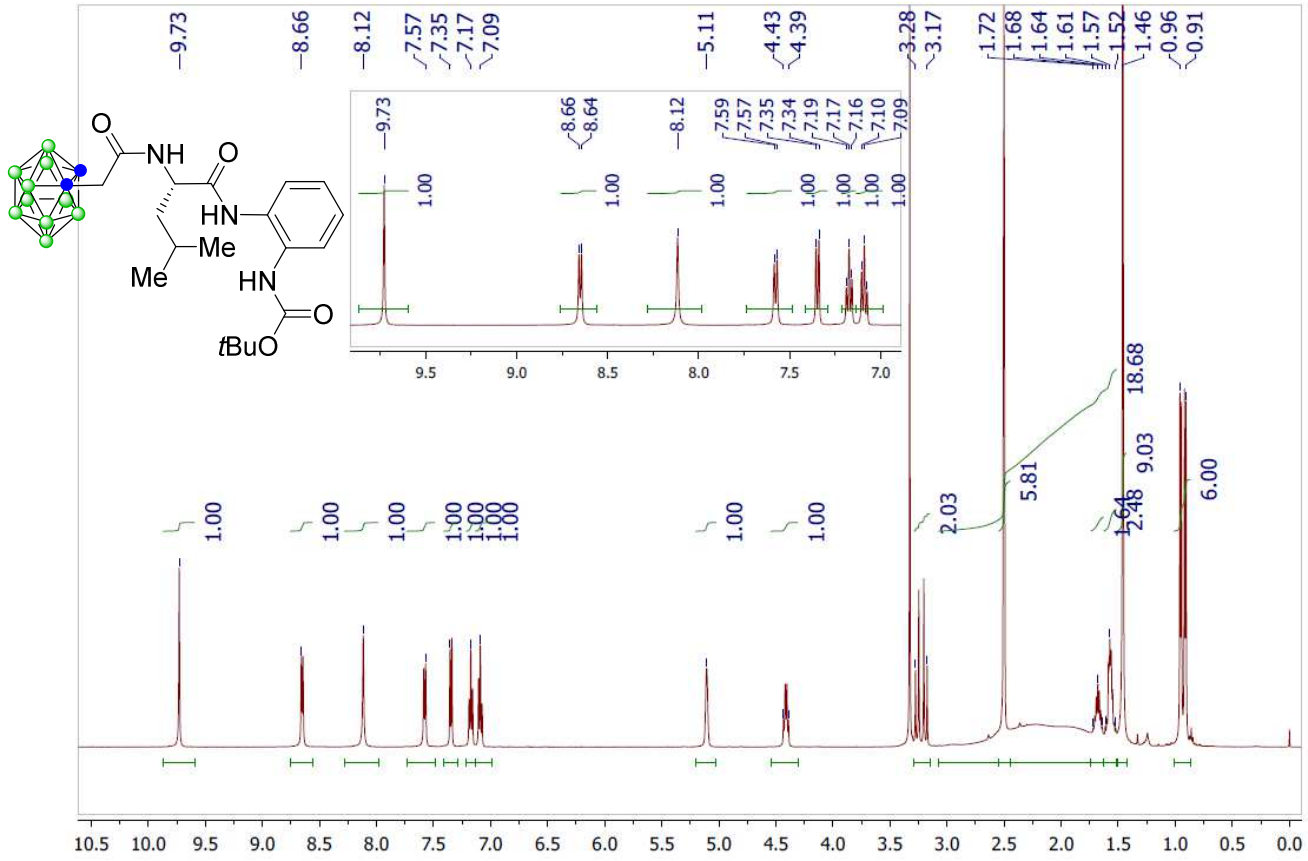
^{1}H NMR spectrum of compound **7c** (***diastereomer II***) (DMSO-d_6, 25 °C, 500 MHz)



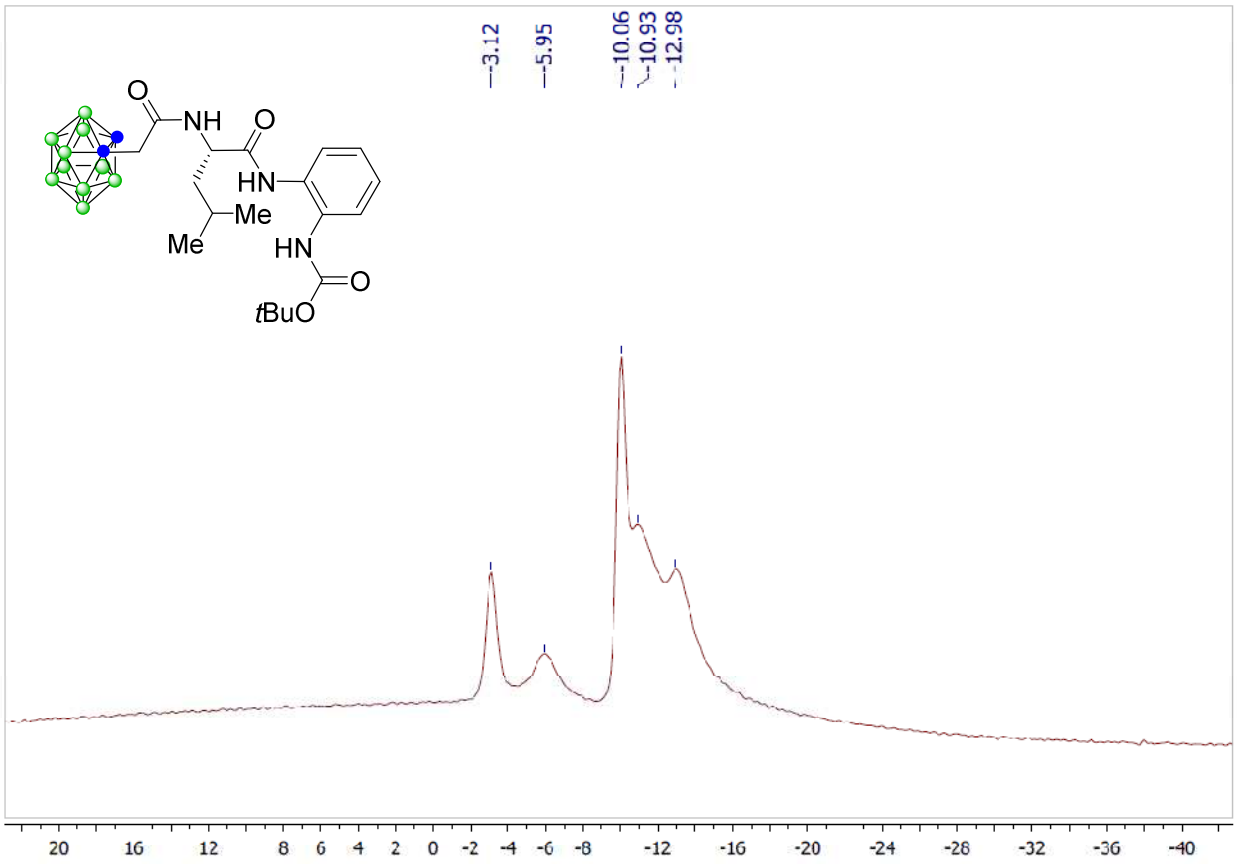
Proton-coupled ^{11}B NMR spectrum of compound **7c** (***diastereomer II***) (DMSO-d_6, 25 °C, 160 MHz)



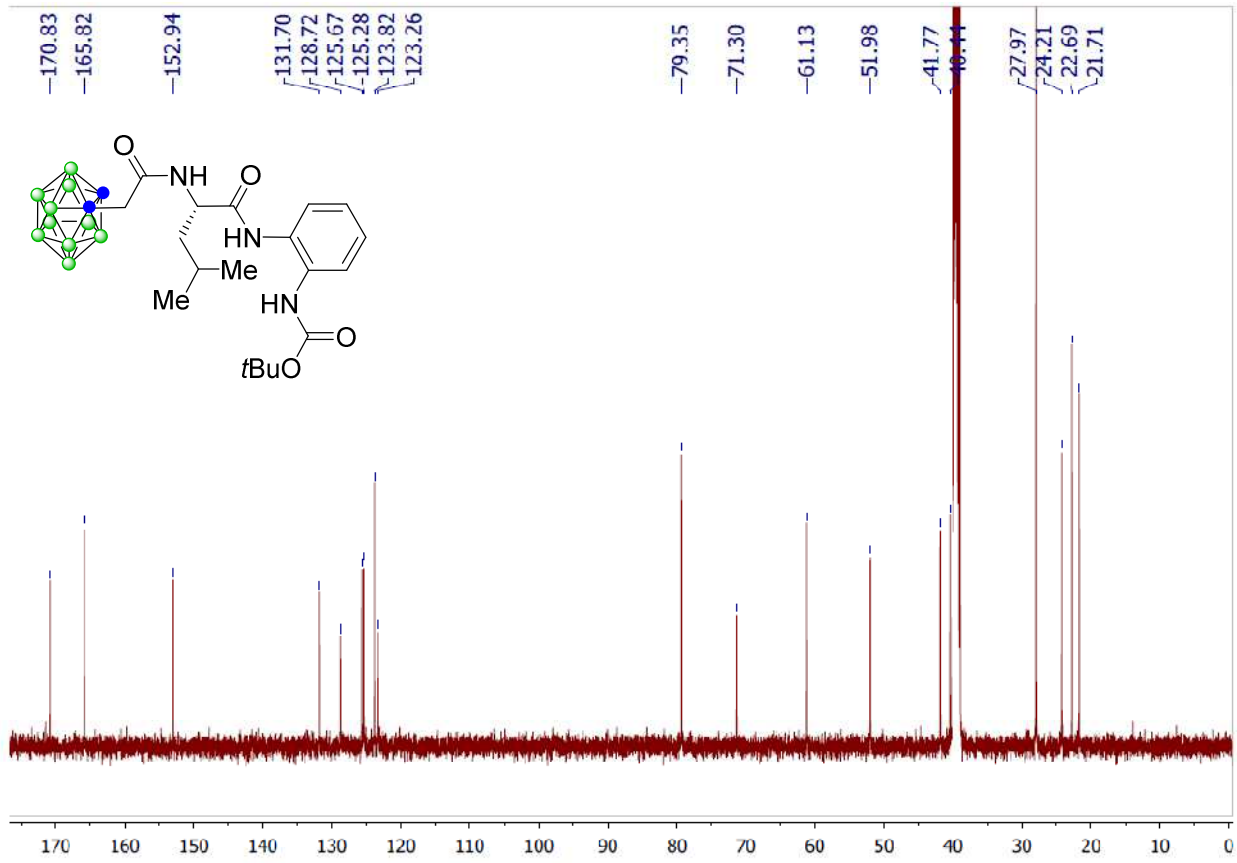
$^{13}C\{^{1}H\}$ NMR spectrum of compound **7c** (***diastereomer II***) (DMSO-d_6, 25 °C, 126 MHz)



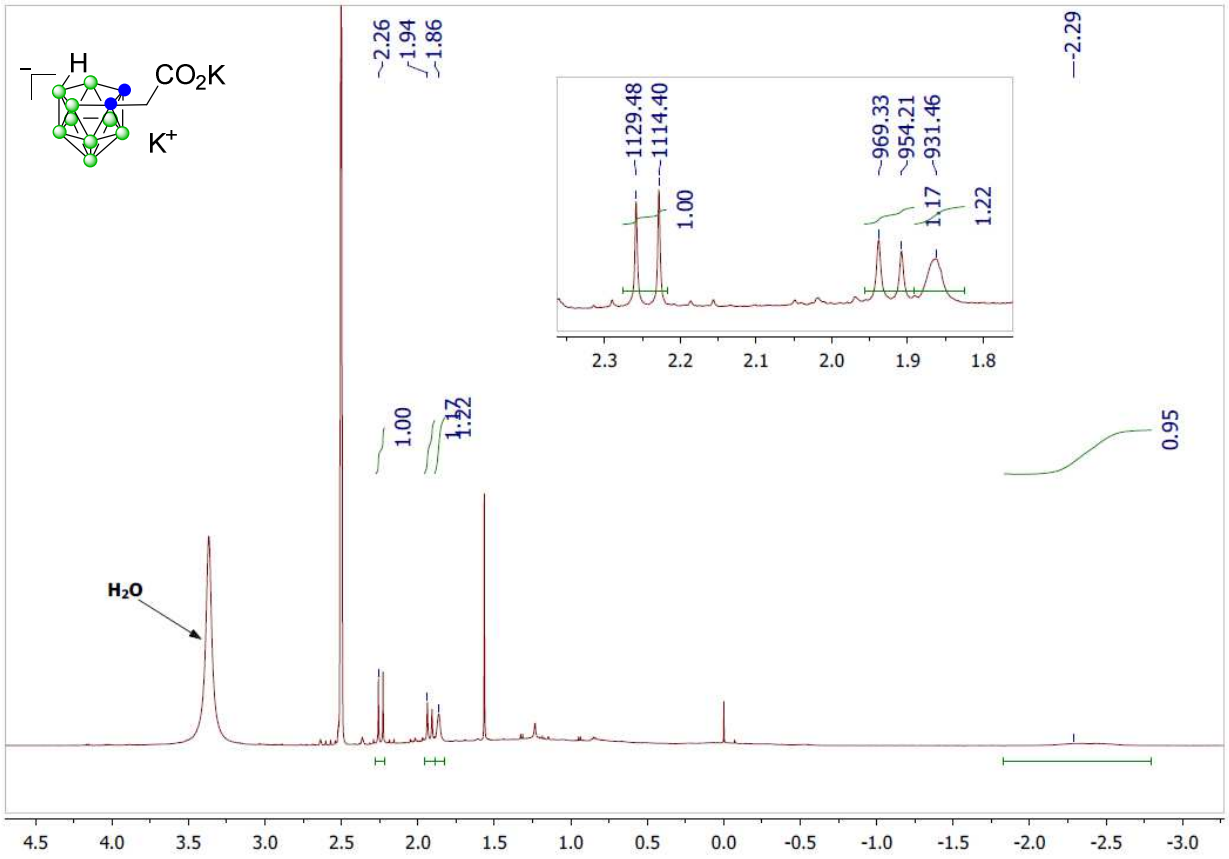
^{1}H NMR spectrum of compound **8** (DMSO-d_6, 25 °C, 500 MHz)



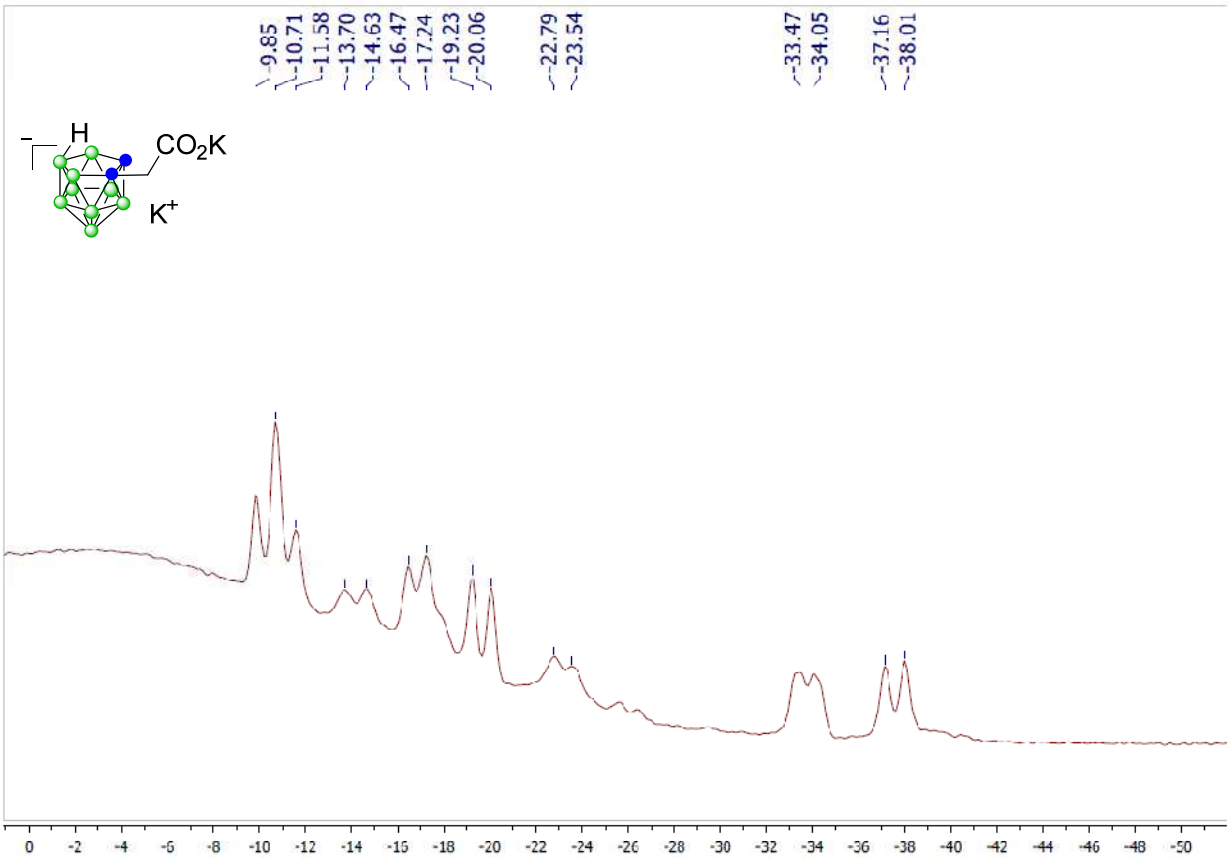
$^{11}B\{^{1}H\}$ NMR spectrum of compound **8** (DMSO-d_6, 25 °C, 160 MHz)



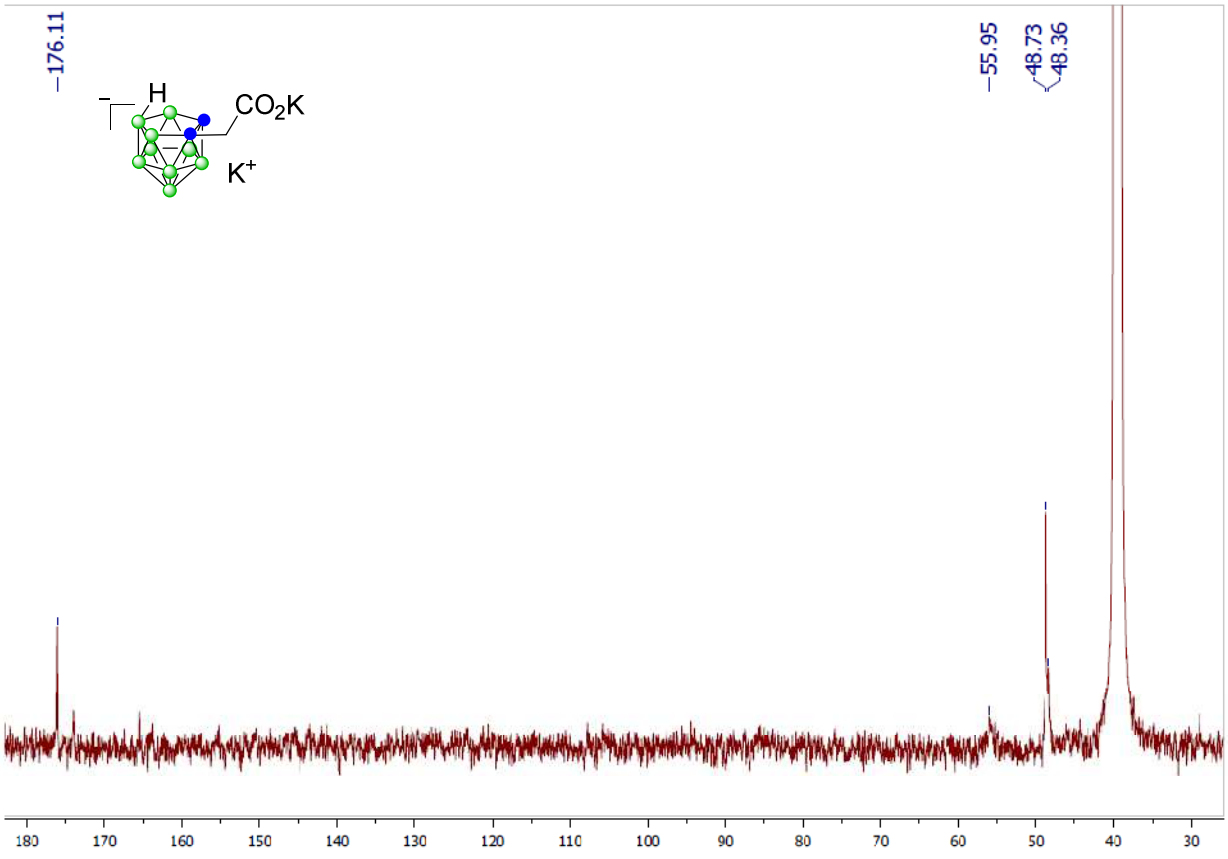
$^{13}C\{^{1}H\}$ NMR spectrum of compound **8** (DMSO-d_6, 25 °C, 126 MHz)



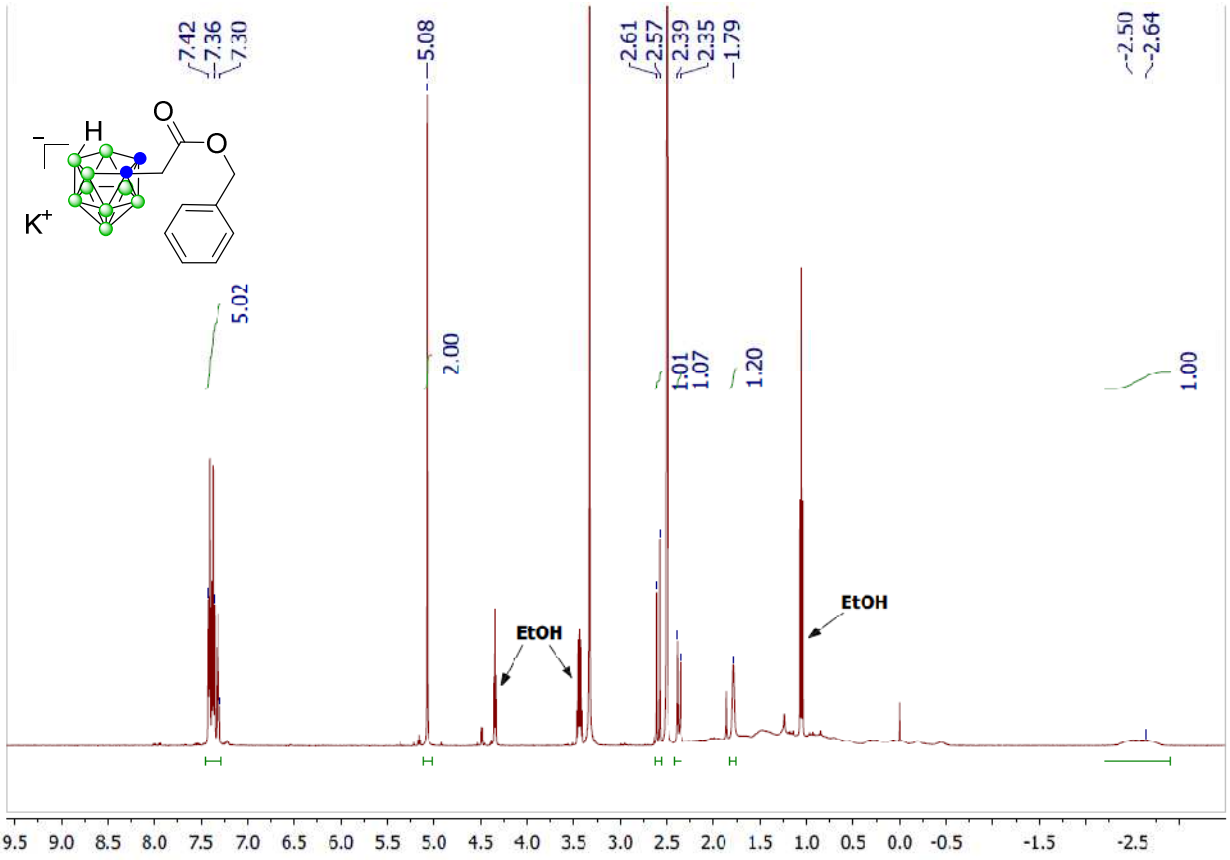
^{1}H NMR spectrum of compound **1-K** (DMSO-d_6, 25 °C, 500 MHz)



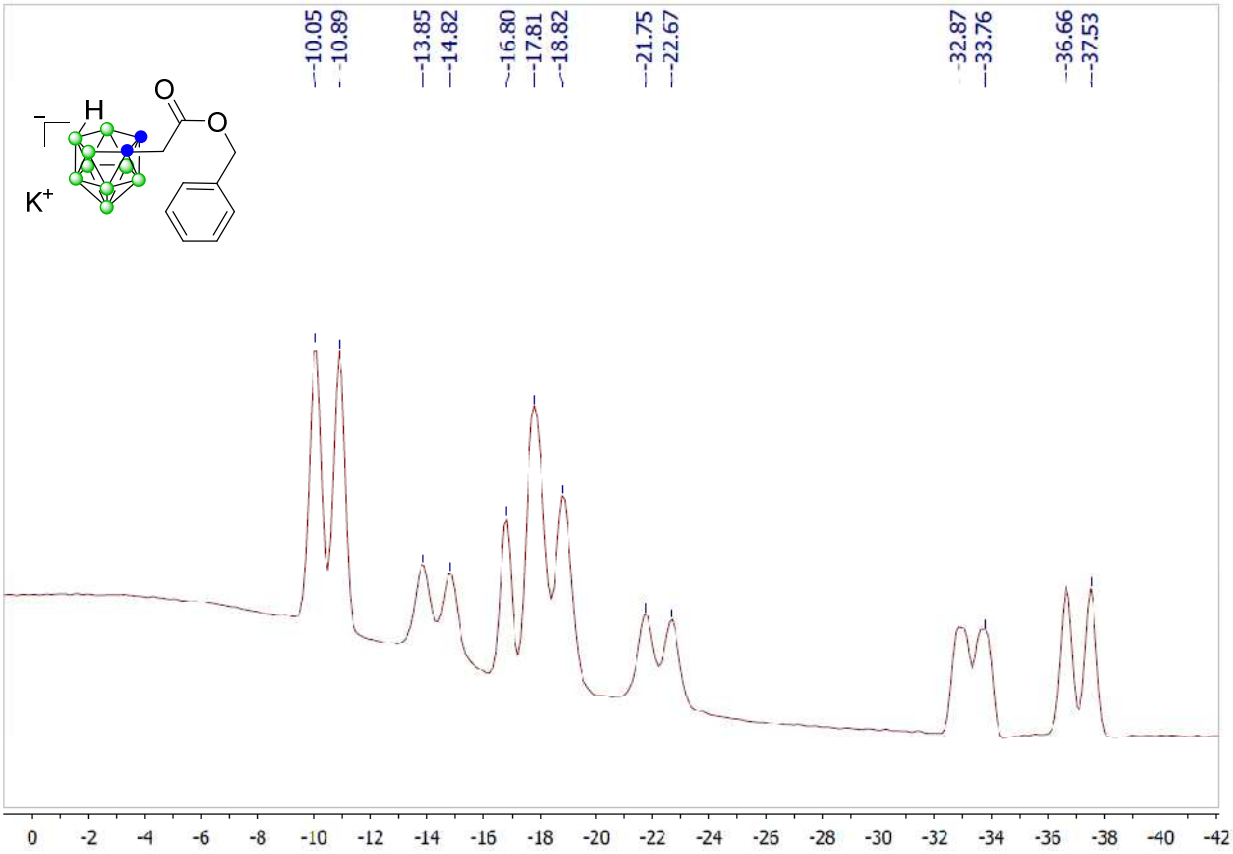
Proton-coupled ^{11}B NMR spectrum of compound **1-K** (DMSO-d_6, 25 °C, 160 MHz)



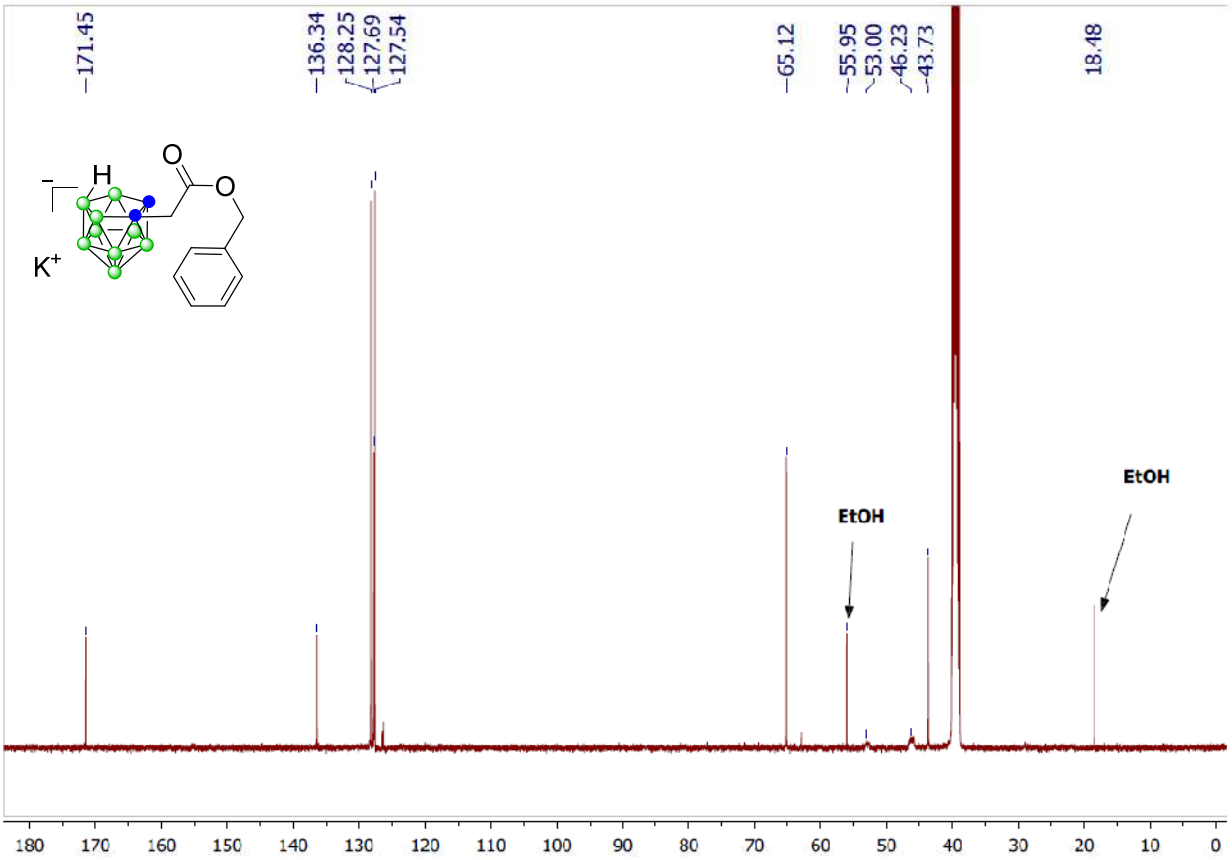
$^{13}C\{^{1}H\}$ NMR spectrum of compound **1-K** (DMSO-d_6, 25 °C, 126 MHz)



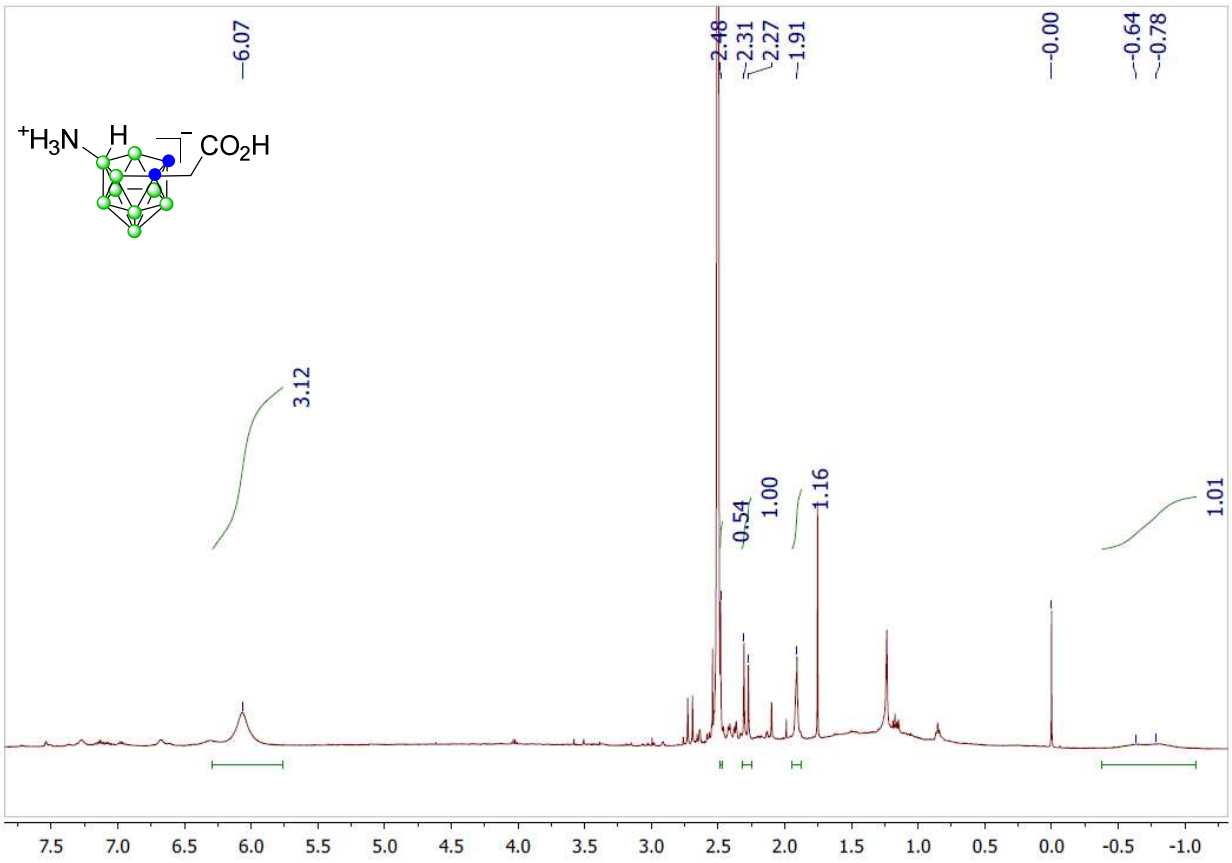
^{1}H NMR spectrum of compound **11-K** (DMSO-d_6, 25 °C, 500 MHz)



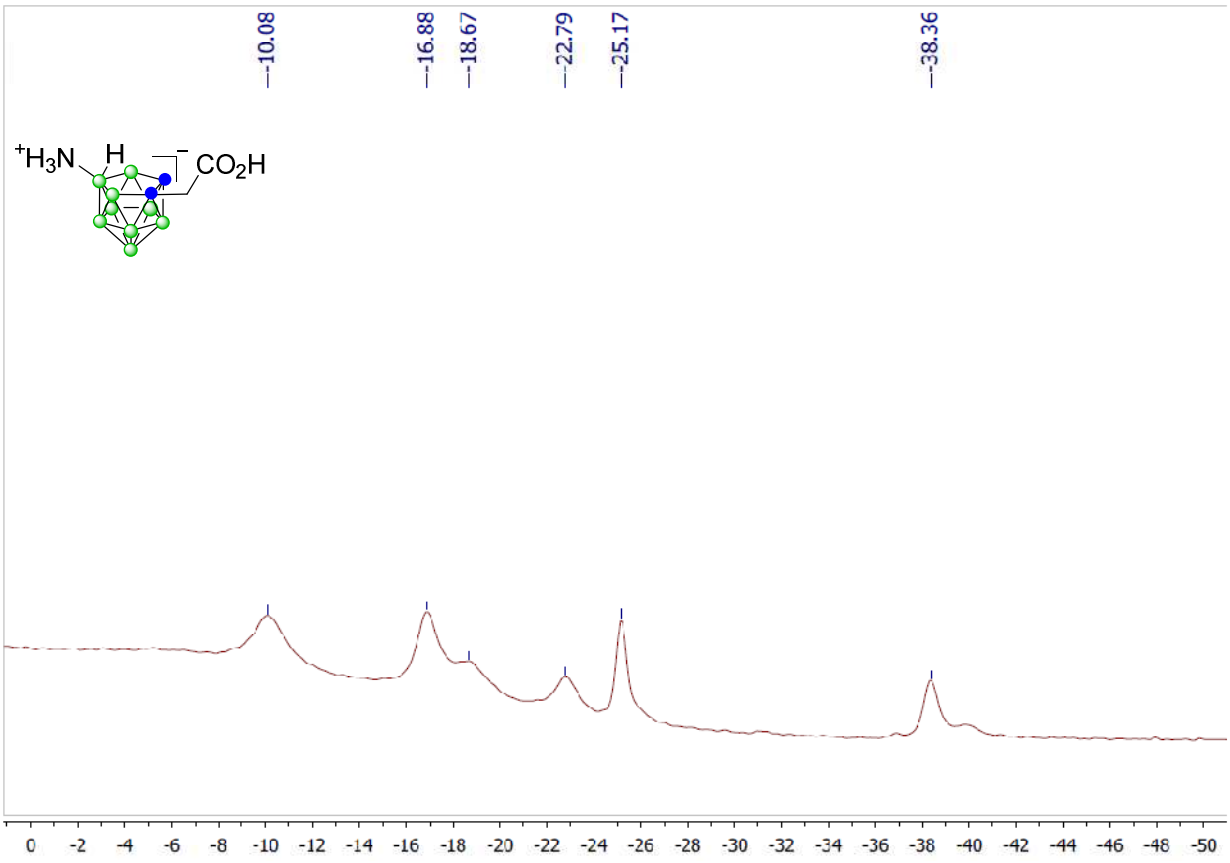
Proton-coupled ^{11}B NMR spectrum of compound **11-K** (DMSO-d_6, 25 °C, 160 MHz)



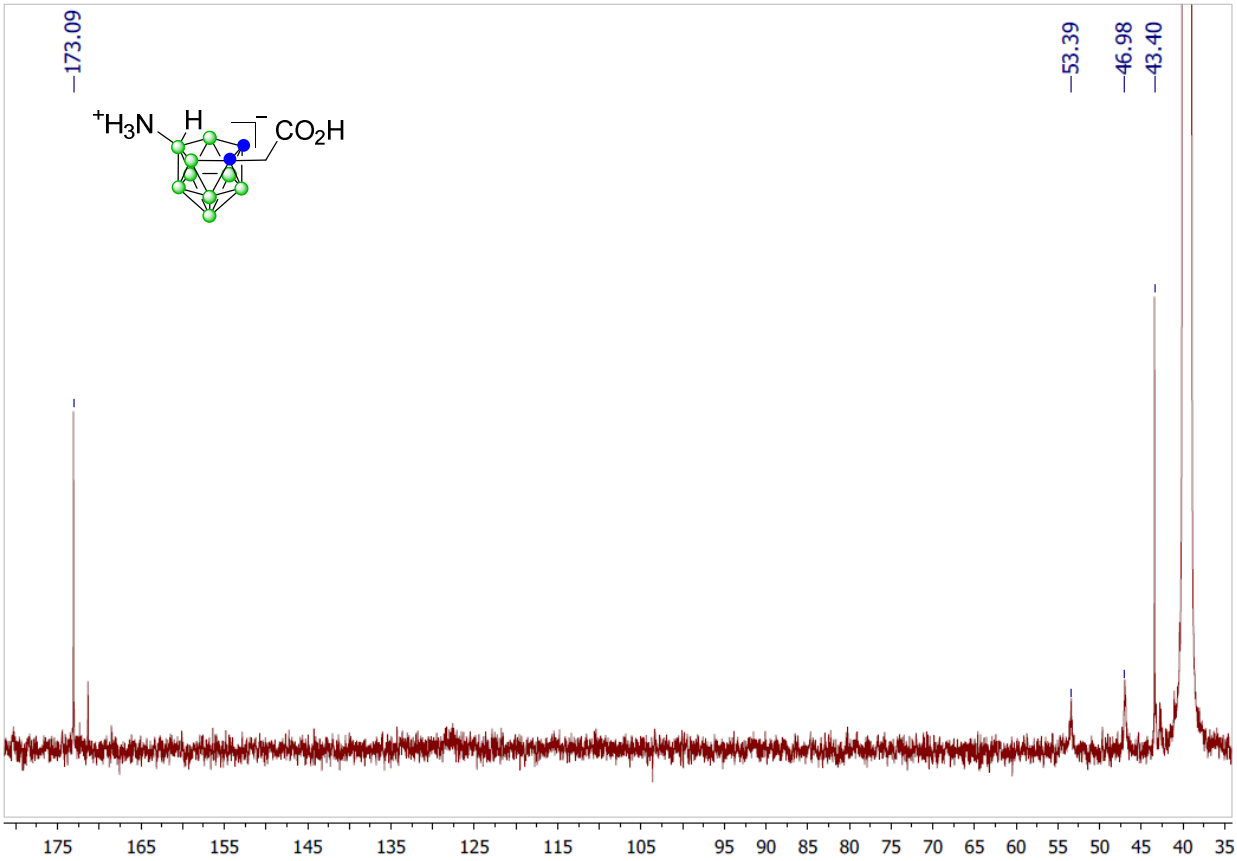
^{13}C{^{1}H} NMR spectrum of compound **11-K** (DMSO-d_6, 25 °C, 126 MHz)



^{1}H NMR spectrum of compound **15** (DMSO-d_6, 25 °C, 500 MHz)

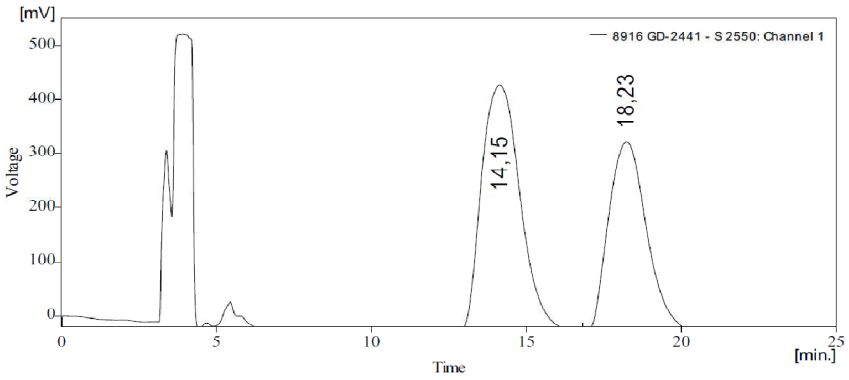


^{11}B{H} NMR spectrum of compound **15** (DMSO-d_6, 25 °C, 160 MHz)



$^{13}C\{^{1}H\}$ NMR spectrum of compound **15** (DMSO-d_6, 25 °C, 126 MHz)

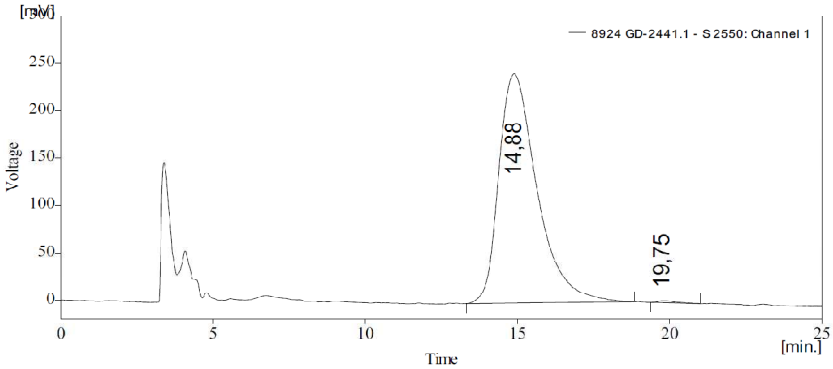
3. Selected HPLC chromatograms



Result Table (Uncal - 8916 GD-2441 - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	14,150	40645,065	461,101	55,8	56,2	1,42
2	18,233	32149,738	359,087	44,2	43,8	1,40
	Total	72794,803	820,188	100,0	100,0	

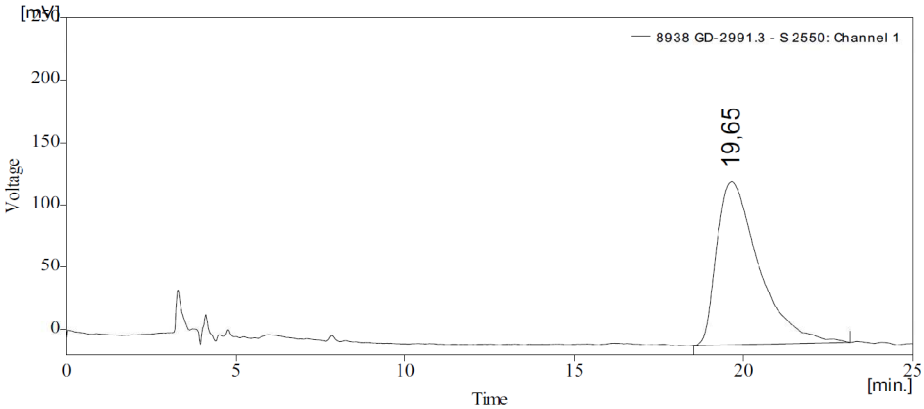
HPLC chromatogram of compound **7a** (*diastereomeric mixture*) (Chiralcel OD-H, *n*-hexane–*i*PrOH–MeOH 5 : 0.8 : 0.2, 1 mL/min)



Result Table (Uncal - 8924 GD-2441.1 - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	14,883	21100,388	242,368	99,6	99,2	1,30
2	19,750	88,966	1,881	0,4	0,8	0,62
	Total	21189,353	244,249	100,0	100,0	

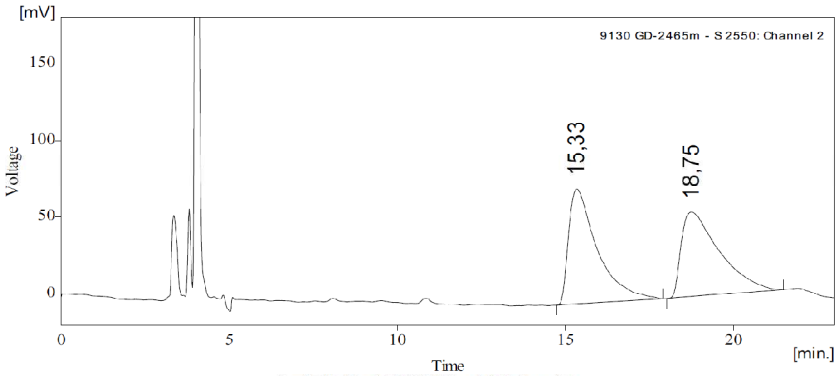
HPLC chromatogram of compound (*S*,R_P)-**7a** (Chiralcel OD-H, *n*-hexane–*i*PrOH–MeOH 5 : 0.8 : 0.2, 1 mL/min)



Result Table (Uncal - 8938 GD-2991.3 - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	19,650	11291,060	130,592	100,0	100,0	1,28
	Total	11291,060	130,592	100,0	100,0	

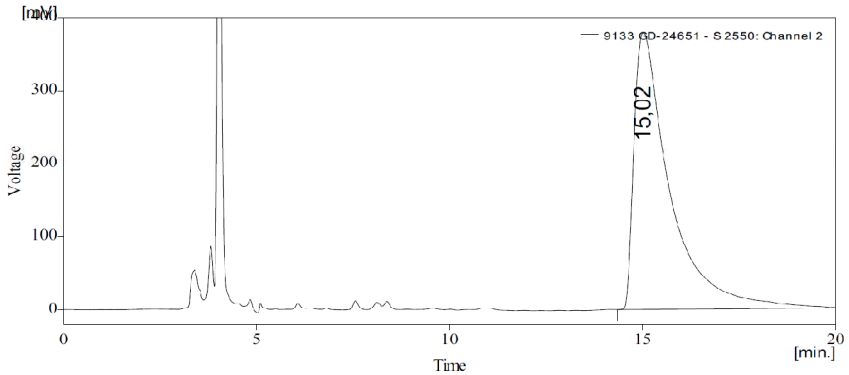
HPLC chromatogram of compound (*S*,S_P)-**7a** (Chiralcel OD-H, *n*-hexane–*i*PrOH–MeOH 5 : 0.8 : 0.2, 1 mL/min)



Result Table (Uncal - 9130 GD-2465m - S 2550: Channel 2)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	15,333	4418,512	74,400	50,4	57,5	0,87
2	18,750	4343,510	55,023	49,6	42,5	1,25
	Total	8762,022	129,423	100,0	100,0	

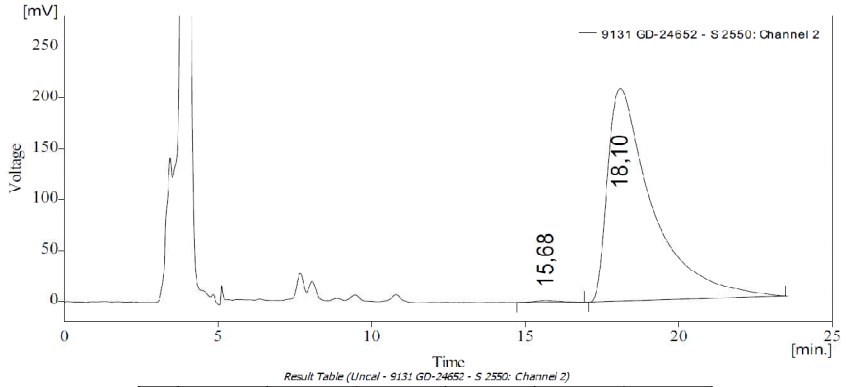
HPLC chromatogram of compound **7b** (*diastereomeric mixture*) (Chiralcel OD-H, *n*-hexane–*i*PrOH–MeOH 50 : 4 : 2, 1 mL/min)



Result Table (Uncal - 9133 GD-24651 - S 2550: Channel 2)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	15,017	24786,960	380,012	100,0	100,0	0,88
	Total	24786,960	380,012	100,0	100,0	

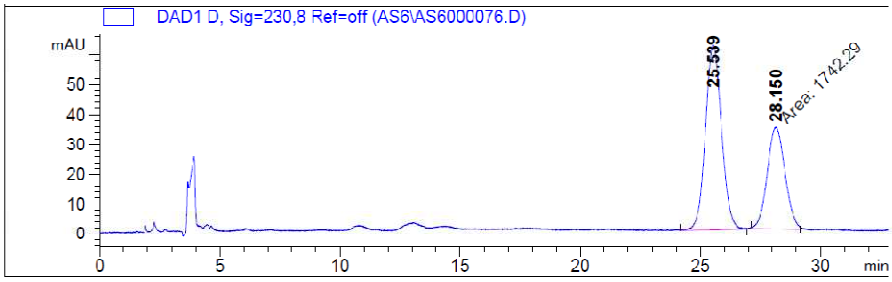
HPLC chromatogram of compound (S,R_P)-**7b** (Chiralcel OD-H, *n*-hexane–*i*PrOH–MeOH 50 : 4 : 2, 1 mL/min)



Result Table (Uncal - 9131 GD-24652 - S 2550: Channel 2)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	15,683	86,336	1,560	0,4	0,7	0,93
2	18,100	21176,248	208,814	99,6	99,3	1,38
	Total	21262,584	210,373	100,0	100,0	

HPLC chromatogram of compound (S,S_P)-**7b** (Chiralcel OD-H, *n*-hexane–*i*PrOH–MeOH 50 : 4 : 2, 1 mL/min)




```
Signal 3: DAD1 D, Sig=230,8 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  25.539 BB    0.6414 2887.20117   61.75583  62.3654
   2  28.150 MM    0.8488 1742.29187   34.21258  37.6346

Totals :                  4629.49304   95.96841

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                        *** End of Report ***
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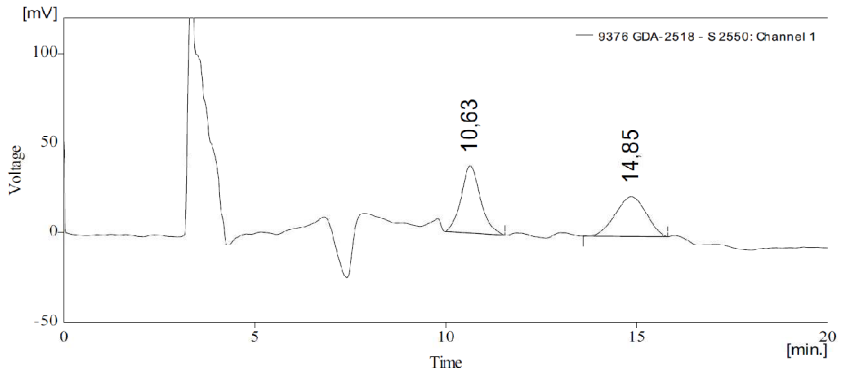
HPLC chromatogram of compound **7c** (*diastereomeric mixture*)
(S,S,-Whelk O1, H_2O–MeOH 55 : 45, 0.8 mL/min)



Result Table (Uncal - 9376 GDA-2518 - S 2550: Channel 1)

	Reten. Time [min]	Area [mAU.s]	Height [mAU]	Area [%]	Height [%]	W05 [min]
1	10,633	1348,069	38,076	51,7	62,8	0,53
2	14,850	1258,838	22,539	48,3	37,2	0,93
	Total	2606,907	60,615	100,0	100,0	

HPLC chromatogram of compound **15** (Chiralcel OD-H, *n*-hexane–*i*PrOH–CF_3CO_2H 5 : 1 : 0.02, 1 mL/min)