

Supplementary information

**Chiral Discrimination of β -Telluride Carboxylic Acids by
NMR Spectroscopy**

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Experimental Considerations

Analytical thin-layer chromatography (TLC) was performed by using aluminum-backed silica plates coated with a 0.25 mm thickness of silica gel 60 F254 (Merck), visualized with an ultraviolet light ($\lambda = 254$ nm), followed by exposure to p-anisaldehyde solution, or vanillin solution and heating.

Standard chromatographic purification methods were followed using 35-70 mm (240-400 mesh) silica gel purchased from Sigma Aldrich®.

Deuterated solvents (99.9% purity with 0.03 % vv of TMS) were purchased from Sigma Aldrich®.

Optical rotations were determined on a Perkin Elmer 341 polarimeter.

IR spectra were obtained on a Bruker Tensor II IR spectrometer as KBr pellets.

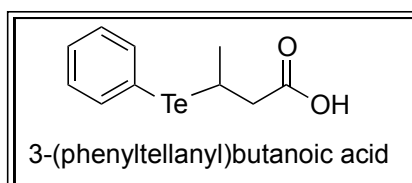
Either 300 MHz or 500 MHz acquired the NMR spectra. The model of NMR equipment – 300MHz Avance III Bruker equipped with a direct BBO probe (broad-band-observed) and 500MHz. Avance III Bruker equipped with an inverse TXI probe (triple-resonance-inversed). The ^1H NMR chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) peak (δ 0.0 ppm). The data are reported as follows: chemical shift (δ), multiplicity (s = singlet, s = broad singlet, d = doublet, t = triplet, q = quadruplet, qt = quintet, st = sextuplet, m = multiplet), features of signal (br = broad, ap = apparent) and coupling constant (J) in Hertz and integrated intensity. The ^{13}C NMR chemical shifts were reported at either 75 or 125 MHz and are reported in ppm relative to CDCl_3 signal (δ 77.0 ppm). The ^{125}Te NMR chemical shifts are reported in ppm relative to internal standard $\text{C}_6\text{H}_5\text{TeTeC}_6\text{H}_5$ (422 ppm).

High-resolution mass spectra (HRMS) were acquired using a Bruker Daltonics MicroTOF instrument, operating electrospray ionization (ESI) mode with ion mass/charge (m/z) ratios as values in atomic mass units.

Typical Procedure for the Lactone Ring Opening Reaction

The organochalcogenide (S, Se and Te) acids were synthesized and characterized as recently described.¹ To a dry two-necked 50 mL round-bottomed flask equipped with magnetic stirring, reflux condenser, and a rubber septum under nitrogen, was added elemental tellurium, selenium or sulfur (4.0 mmol) previously dried overnight in an oven at 100 °C. Then dry tetrahydrofuran (15 mL) was added. To the stirred suspension was added the respective organometallic compound (*n*-butyllithium or phenylmagnesium chloride). The mixture was then stirred by 30 minutes and the lactone (2.6mmol) was added all at once. The reaction was monitored by gas chromatography. After 1 h at room temperature the reaction medium was diluted with AcOEt (20 mL) and washed with saturated solution of NH₄Cl (15 mL). The phases were separated and the aqueous phase was extracted with AcOEt (2 x 20 mL). The organic phase was dried over MgSO₄ and the solvents were evaporated under reduced pressure. The residue was purified by flash column chromatography eluting first with hexane to remove alkyl or aryl byproducts and then with hexane/AcOEt (8:2) to remove the product.

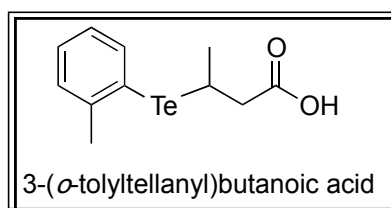
Spectral data of compound **1a**:



Red oil, 88 % yield. ¹H NMR (500MHz, CDCl₃, 25 °C, TMS, δ ppm): 7.82-7.84 (m, 2H); 7.32-7.36 (m, 1H); 7.22-7.26 (m, 2H); 3.65 (st, *J* = 7.15 Hz, 1H); 2.86 (dd, *J* = 6.75 Hz and 16.4 Hz, 1H); 2.82 (dd, *J* = 7.7 Hz and 16.4 Hz, 1H); 1.64 (d, *J* = 7.15 Hz, 3H). ¹³C NMR (75MHz, CDCl₃, 25 °C, TMS, δ ppm): 178.0, 140.8, 129.2, 128.4, 111.2, 44.5, 24.2, 14.2. ¹²⁵Te NMR (94.74 MHz, CDCl₃, 25 °C, C₆H₅TeTeH₅C₆ standard δ ppm 422): 709.4. IR (cm⁻¹): 3064, 1954, 1881, 1573, 1140, 1107, 1074, 1017, 998, 930, 908, 655, 613, 484, 455. HR-MS: Calculated value: 293.9899; Found value [M⁺]: 294.9912.

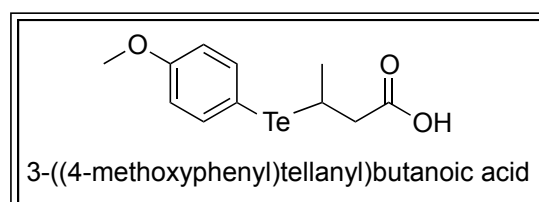
¹ (a) Silva, M. S.; Dos Santos, A. A.; Comasseto, J. V. *Tetrahedron Lett.* **2009**, *50*, 6498-6501; Node, M.; Nishide, K.; Ochiai, M.; Fuji, K.; Fujita, E. *J. Org. Chem.* **1981**, *46*, 5163-5166; (c) Liotta, D.; Sunay, U.; Santiesteban, E.; Markiewicz, W. *J. Org. Chem.* **1981**, *46*, 2605-2610; (d) Menezes, P. H.; Gonçalves, S. M. C.; Hallwass, F.; Silva, R. O.; Bieber, L. W.; Simas, A. M. *Org. Lett.* **2003**, *5*, 1601-1604.

Spectral data of compound **1b**:



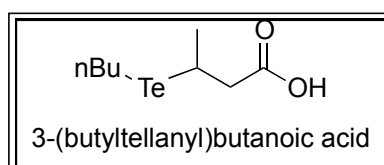
Red oil, 91 % yield. $^1\text{H NMR}$ (300MHz, CDCl_3 , 25 °C, TMS, δ ppm): 7.81 (d, $J = 7.44$ Hz, 1H); 7.20-7.29 (m, 2H); 7.02 (dt, $J = 1.47$ Hz, and 7.44 Hz, 1H); 3.70 (st, $J = 7.14$ Hz, 1H); 2.85 (m, 1H); 2.83 (d, $J = 1.89$ Hz, 1H); 2.51 (s, 3H); 1.64 (d, $J = 7.11$ Hz, 3H). $^{13}\text{C NMR}$ (75MHz, CDCl_3 , 25 °C, TMS, δ ppm): 178.3, 143.8, 140.6, 129.0, 128.9, 126.6, 116.3, 44.5, 27.6, 24.0, 14.0. **IR** (cm^{-1}): 3053, 2862, 2731, 2627, 1565, 1341, 1075, 1049, 989, 931, 909, 796, 705, 648, 603, 539, 477, 403. **HR-MS**: Calculated value: 308.0056; Found value [$\text{M}^+ + 1$]: 309.011.

Spectral data of compound **1c**:



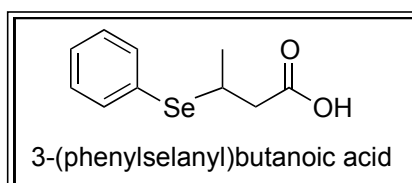
Red crystals, 79 % yield. $^1\text{H NMR}$ (300MHz, CDCl_3 , 25 °C, TMS, δ ppm): 7.74 (dd, $J = 2.07$ Hz and 6.63 Hz, 2H); 6.78 (dd, $J = 2.07$ Hz and 6.63 Hz, 2H); 3.56 (st, $J = 7.14$ Hz, 1H); 2.80 (d, $J = 0.63$ Hz and 1.44 Hz, 1H); 1.59 (d, $J = 7.14$ Hz, 3H). $^{13}\text{C NMR}$ (75MHz, CDCl_3 , 25 °C, TMS, δ ppm): 178.1, 160.2, 143.0, 115.1, 100.3, 55.1, 44.5, 24.1, 13.9. **IR** (cm^{-1}): 3433, 3016, 2857, 2732, 2066, 1967, 1835, 1563, 1461, 1397, 1340, 1133, 1102, 1064, 997, 911, 886, 789, 622, 588, 496, 418. **HR-MS**: Calculated value: 324.0005; Found value [$\text{M}^+ + 1$]: 325.9976.

Spectral data of compound **1d**:



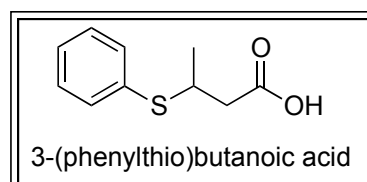
Red oil, 68 % yield. $^1\text{H NMR}$ (500MHz, CDCl_3 , 25 °C, TMS, δ ppm): 3.48 (st, $J = 7.15$ Hz, 1H); 2.86 (tap, $J = 6.65$ Hz, 2H); 2.73 (dtap, $J = 7.4$ and 3.1 Hz, 2H); 1.78 (qt, $J = 7.45$ Hz, 2H); 1.68 (d, $J = 7.2$ Hz, 3H); 1.38 (st, $J = 7.45$ Hz, 2H); 0.92 (t, $J = 7.45$ Hz, 3H). $^{13}\text{C NMR}$ (75MHz, CDCl_3 , 25 °C, TMS, δ ppm): 178.3, 45.4, 34.4, 25.3, 24.9, 13.4, 8.5, 3.5. **IR** (cm^{-1}): 2926, 2730, 1164, 1105, 1074, 990, 889, 769, 604, 496. **HR-MS**: Calculated value: 274.0212; Found value [$\text{M}^+ + 1$]: 275.0156.

Spectral data of compound **1e**:



Yellow oil, 83 % yield. $^1\text{H NMR}$ (500MHz, CDCl_3 , 25 °C, TMS, δ ppm): 7.57-7.59 (m, 2H); 7.25-7.31 (m, 3H); 3.62 (st, $J = 6.85$ Hz, 1H); 2.73 (dd, $J = 6.3$ Hz and 16.1 Hz, 1H); 2.61 (dd, $J = 4.0$ Hz and 16.1 Hz, 1H); 1.46 (d, $J = 6.9$ Hz, 3H). $^{13}\text{C NMR}$ (75MHz, CDCl_3 , 25 °C, TMS, δ ppm): 177.5, 135.7, 129.1, 128.1, 127.8, 42.4, 33.2, 21.8. **IR** (cm^{-1}): 3071, 2731, 1952, 1880, 1605, 1595, 1499, 1377, 1110, 931, 813, 671, 471. **HR-MS**: Calculated value: 244.0002; Found value [$\text{M}^+ + 1$]: 245.9987.

Spectral data of compound **1f**:



Pale yellow oil, 71 % yield. $^1\text{H NMR}$ (500MHz, CDCl_3 , 25 °C, TMS, δ ppm): 7.43-7.46 (m, 2H); 7.26-7.33 (m, 3H); 3.6 (st, $J = 6.8$ Hz, 1H); 2.69 (dd, $J = 15.95$ and 5.9 Hz, 1H); 2.48 (dd, $J = 15.95$ and 8.45 Hz, 1H); 1.36 (d, $J = 6.8$ Hz, 3H). $^{13}\text{C NMR}$ (125MHz, CDCl_3 , 25 °C, TMS, δ ppm): 176.6, 133.5, 133.1, 129.0, 126.7, 41.4, 39.2, 20.8. **IR** (cm^{-1}): 3074, 2872, 2669, 1584, 1477, 1377, 1179, 1092, 1069, 1001, 931, 649, 521, 483. **HR-MS**: Calculated value: 196.0558; Found value [$\text{M}^+ + 1$]: 197.0582.

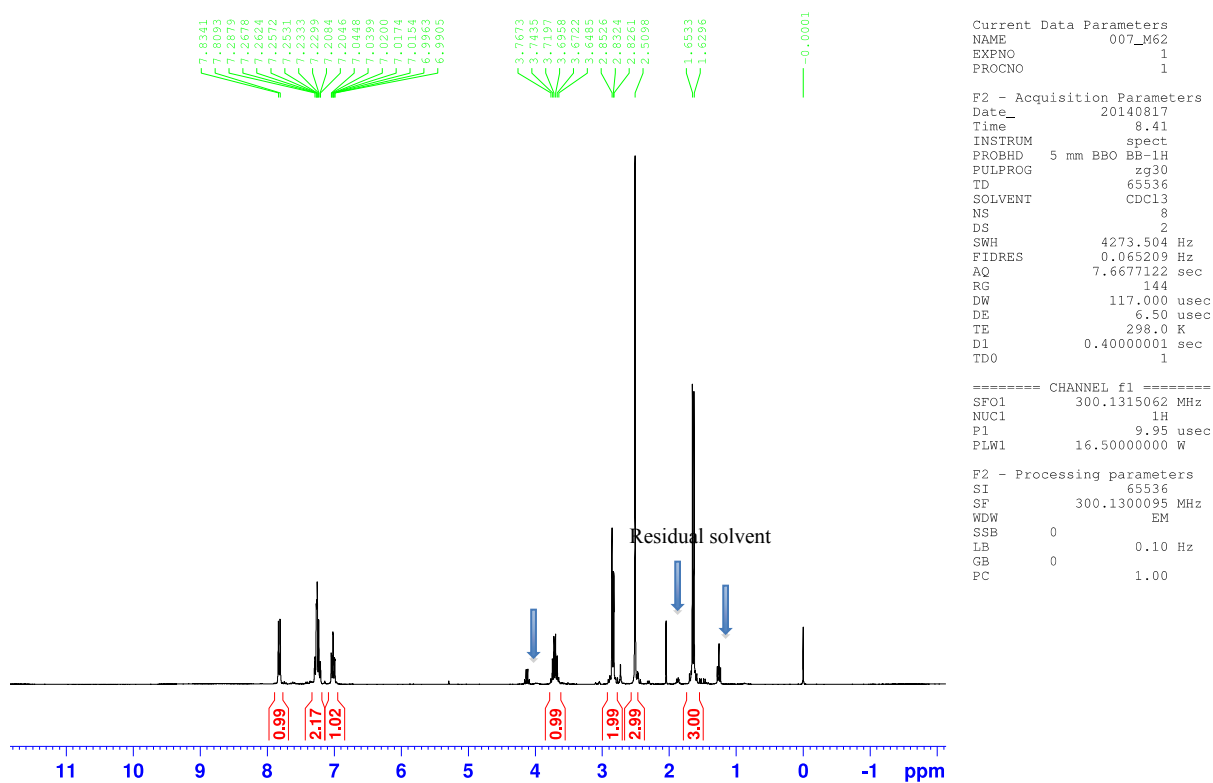


Figure S3: ^1H NMR spectrum of organochalcogenide acid **1b** in CDCl_3 at 25 $^\circ\text{C}$

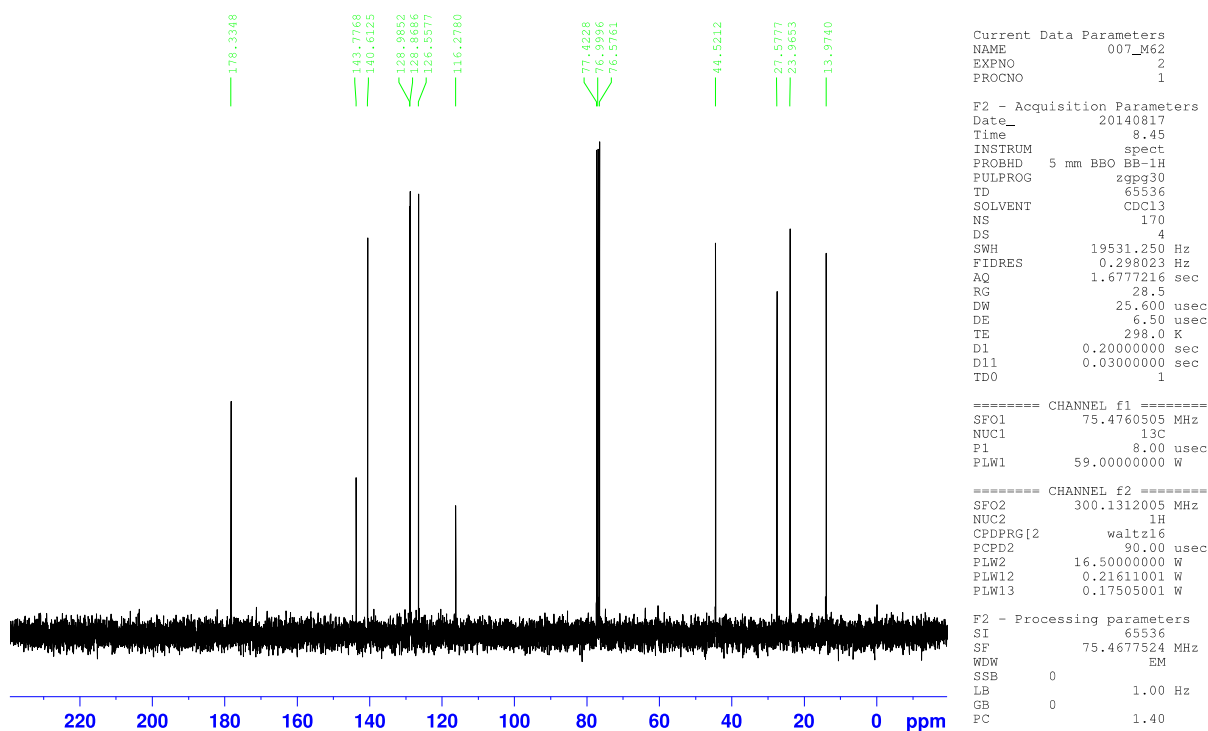


Figure S4: ^{13}C NMR spectrum of organochalcogenide acid **1b** in CDCl_3 at 25 $^\circ\text{C}$

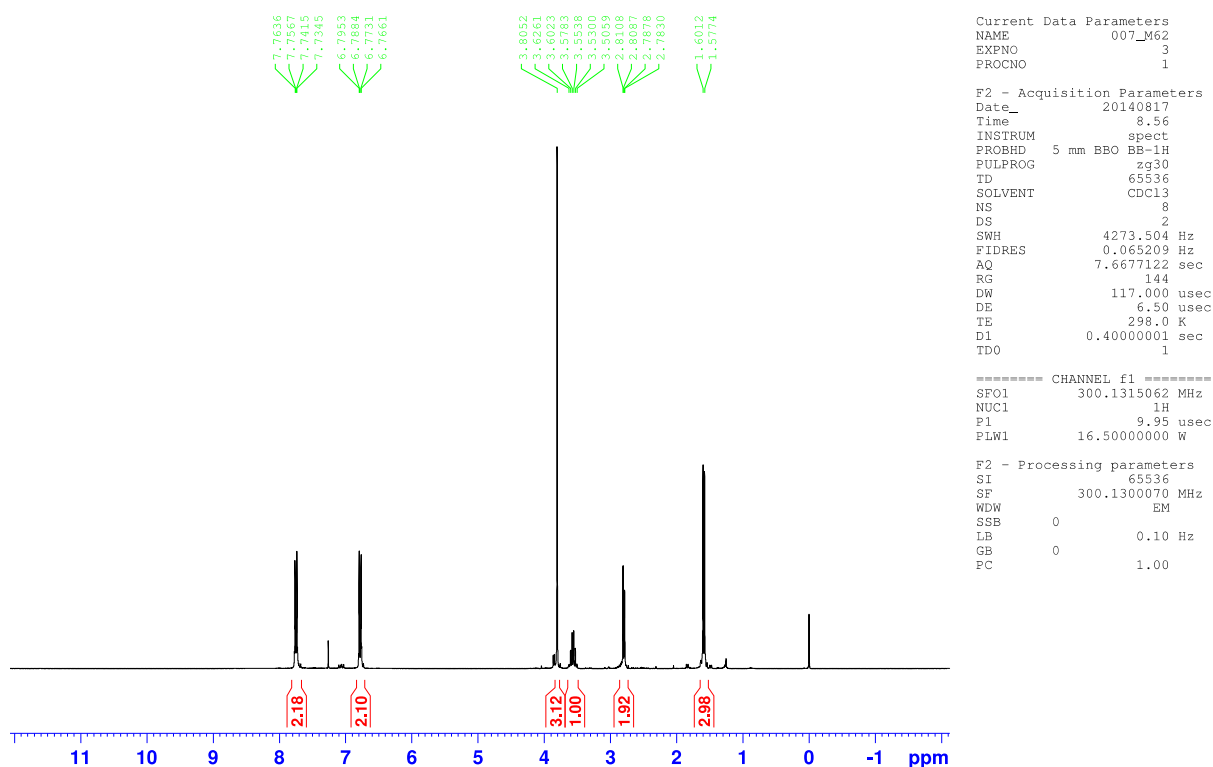


Figure S5: ^1H NMR spectrum of organochalcogenide acid **1c** in CDCl_3 at 25 $^\circ\text{C}$

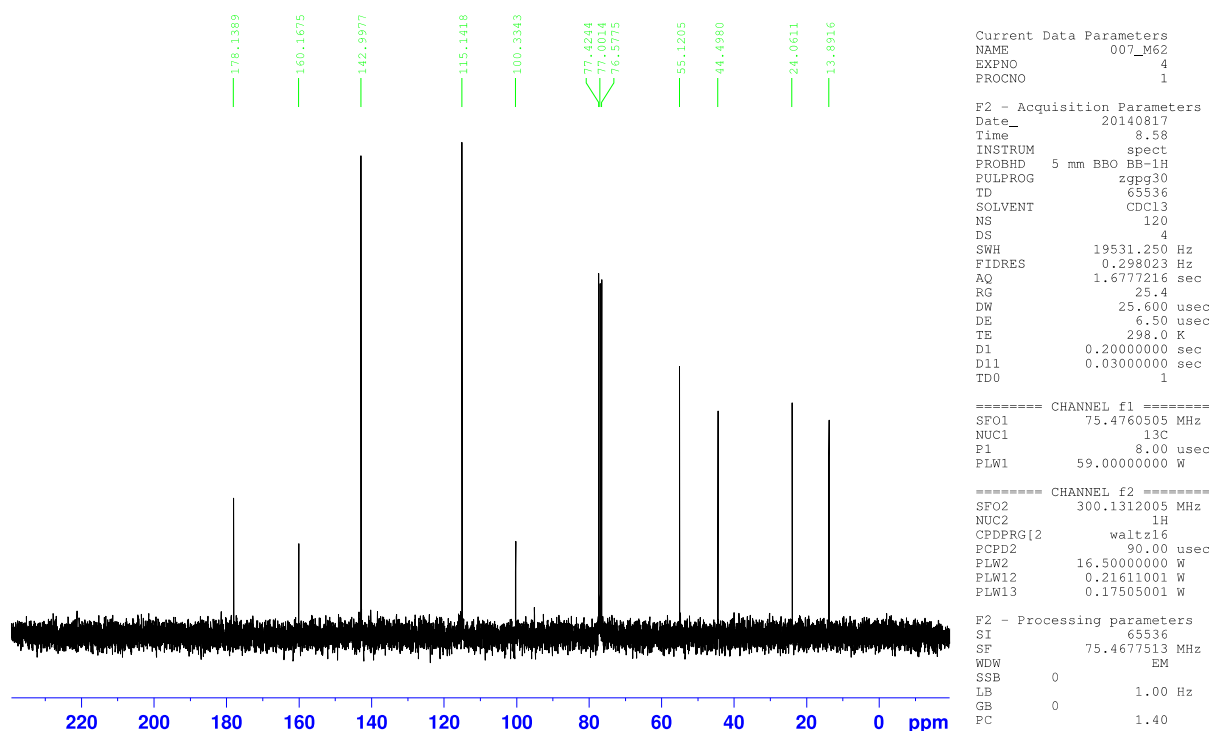


Figure S6: ^{13}C NMR spectrum of organochalcogenide acid **1c** in CDCl_3 at 25 $^\circ\text{C}$

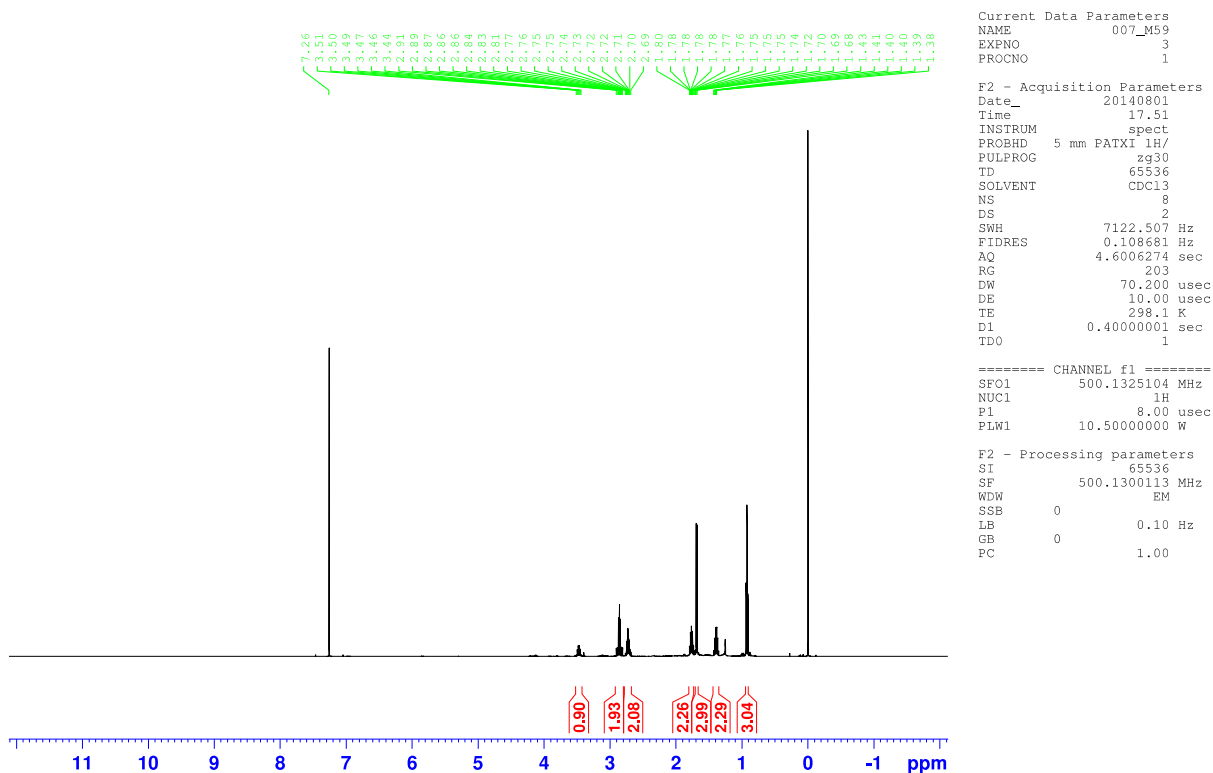


Figure S7: ^1H NMR spectrum of organochalcogenide acid **1d** in CDCl_3 at 25 $^\circ\text{C}$

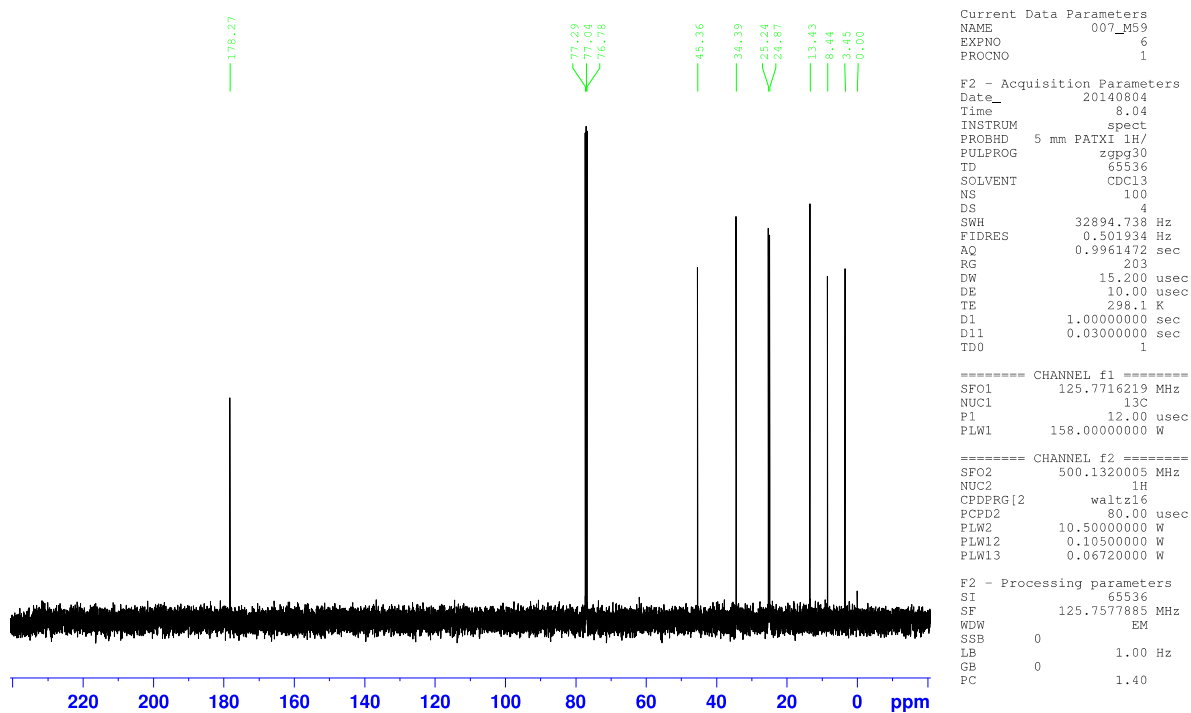


Figure S8: ^{13}C NMR spectrum of organochalcogenide acid **1d** in CDCl_3 at 25 $^\circ\text{C}$

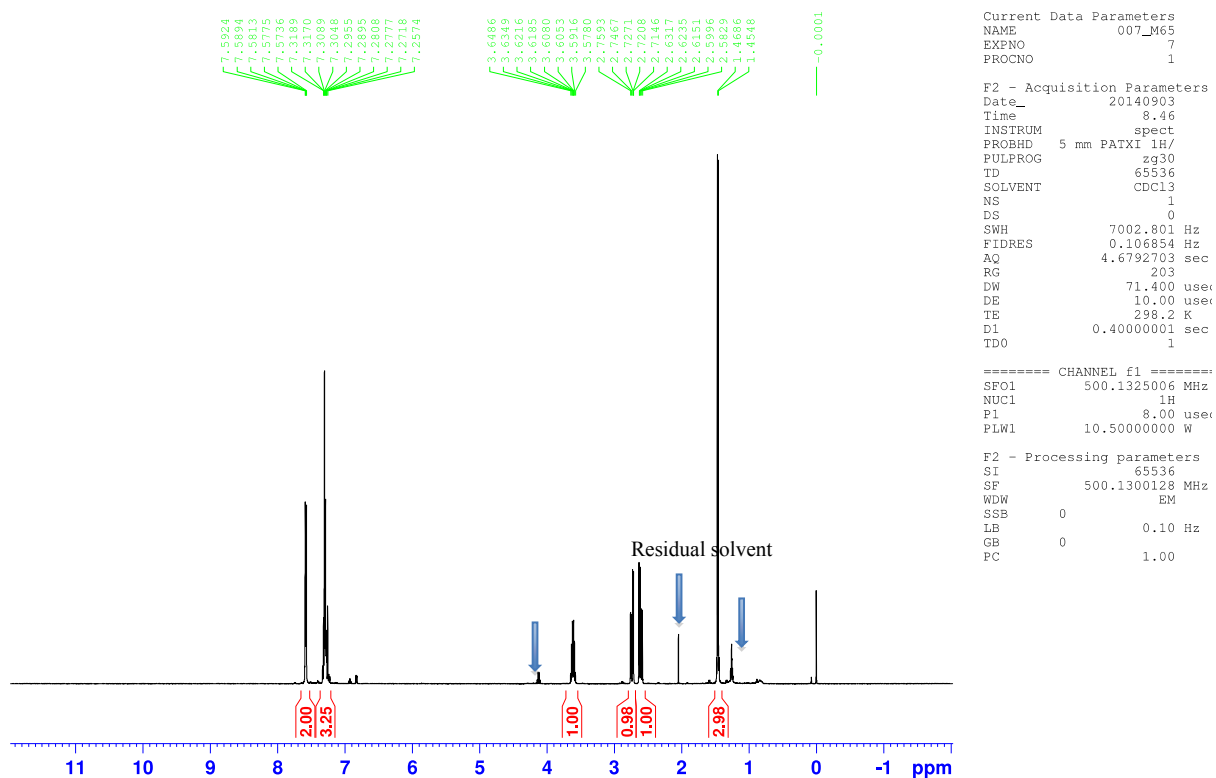


Figure S9: ^1H NMR spectrum of organochalcogenide acid **1e** in CDCl_3 at $25\text{ }^\circ\text{C}$

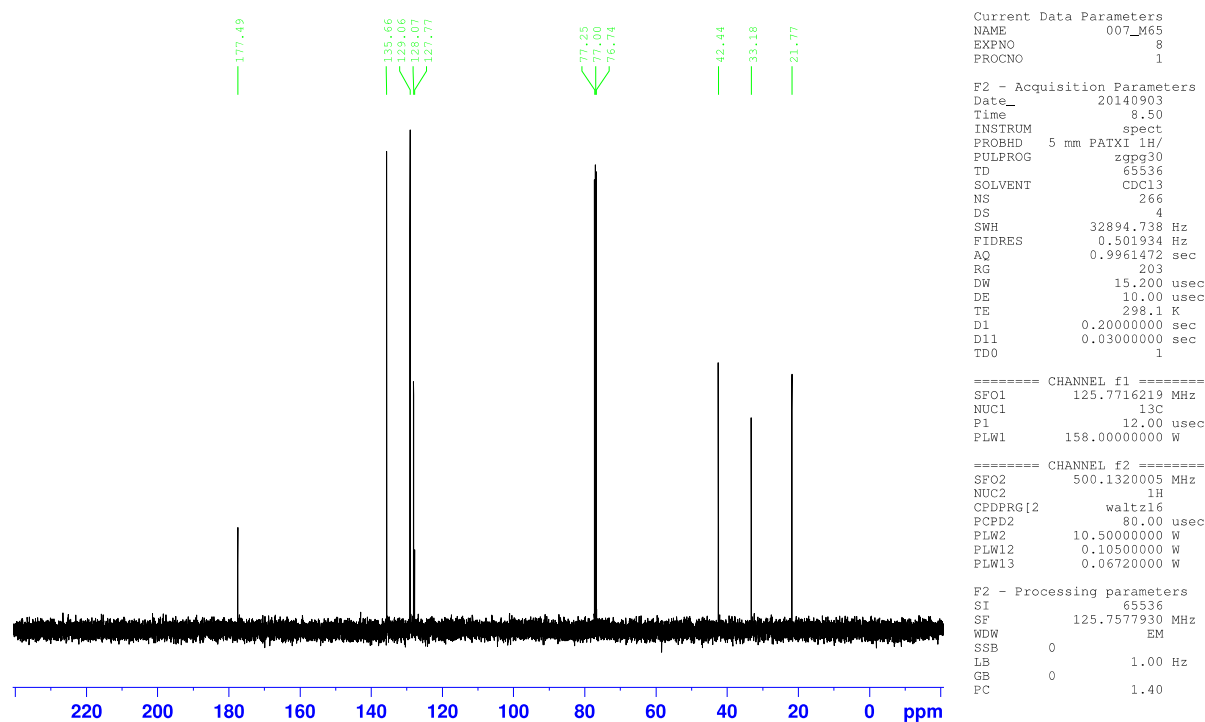


Figure S10: ^{13}C NMR spectrum of organochalcogenide acid **1e** in CDCl_3 at $25\text{ }^\circ\text{C}$

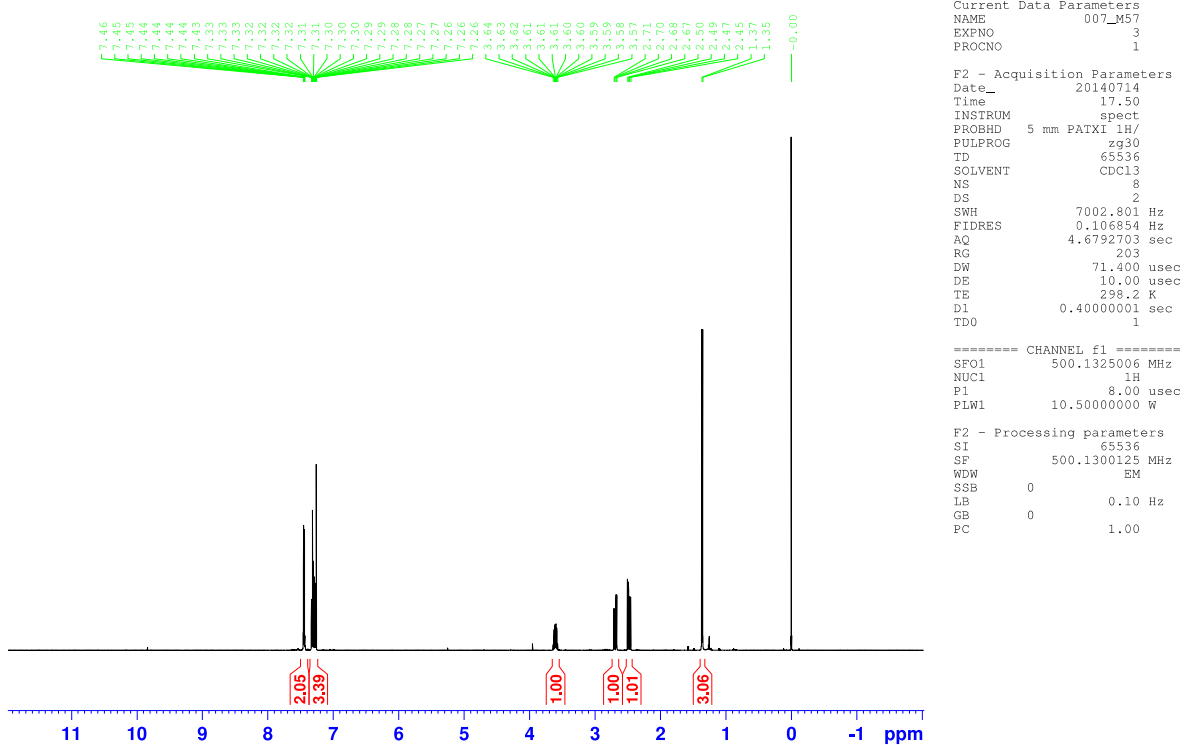


Figure S11: ^1H NMR spectrum of organochalcogenide acid **1f** in CDCl_3 at 25 °C

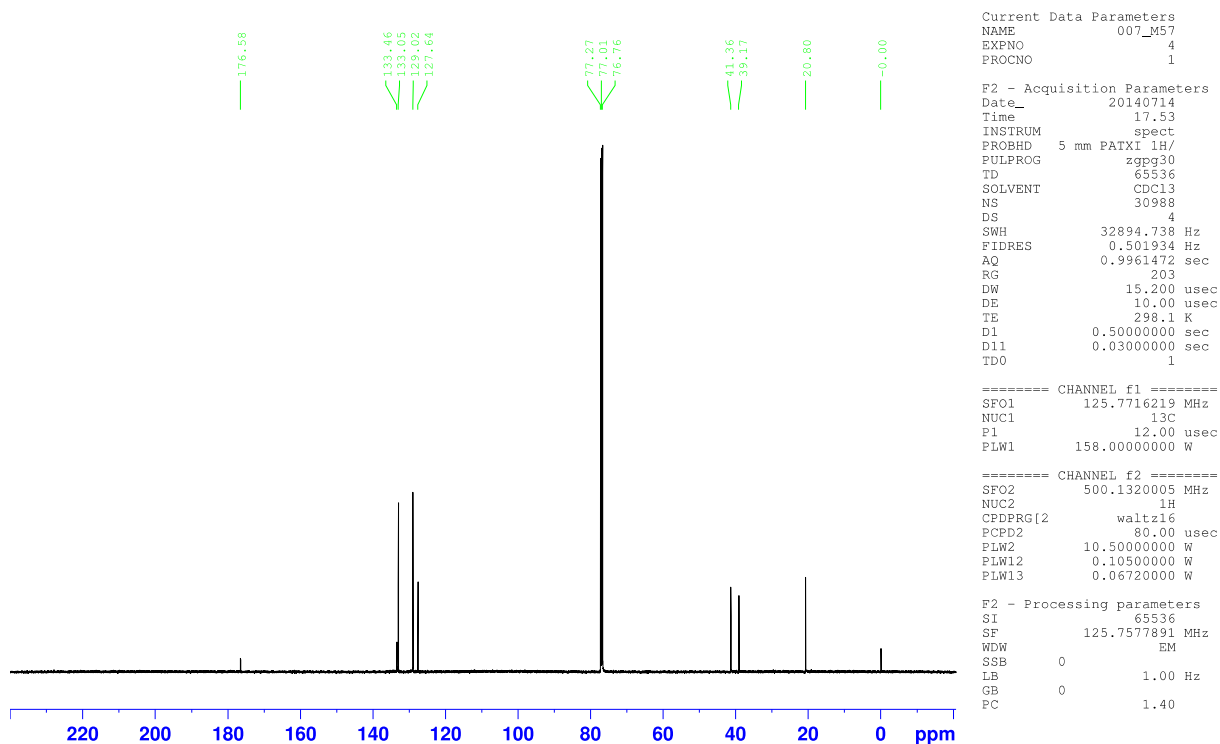
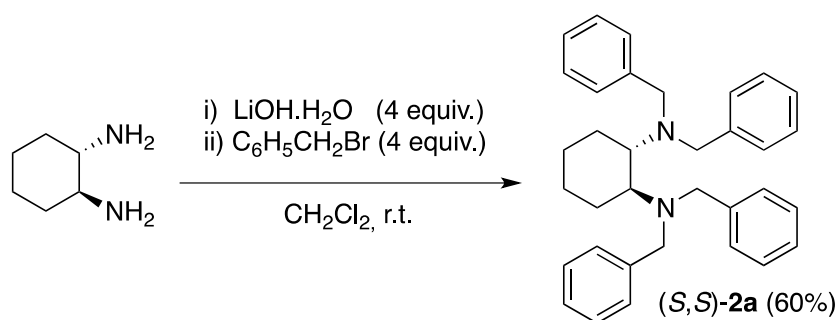


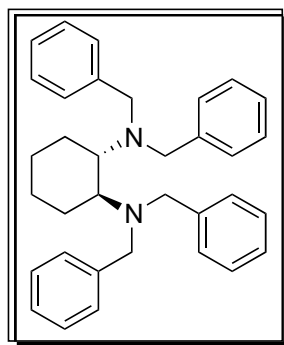
Figure S12: ^{13}C NMR spectrum of organochalcogenide acid **1f** in CDCl_3 at 25 °C

Typical procedure for the synthesis of tetrabenzyl cyclohexyl-1,2-diamine



The tetrabenzyl cyclohexyl-1,2-diamine **2a** was synthesized and characterized as recently described.² The cyclohexyl-1,2-diamine (1.0 mmol) was added to 50 mL round-bottomed flask equipped with magnetic stirring, 25 mL of CH₂Cl₂ and a rubber septum under nitrogen. Afterward, the LiOH.H₂O (4.0 mmol) and benzyl bromide (4.0 mmol) were added to the flask. The solution was stirred for a further 8 hours. Water (10 mL) was added. The aqueous layer was washed with dichloro-methane (2 x 50 mL) and the combined organic extracts were dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography hexan/AcOEt (9:1).

Spectral data of compound **2a**:



(1S,2S)-N1,N1,N2,N2-tetrabenzylcyclohexane-1,2-diamine

White crystals, 60 % yield. ¹H NMR (500 MHz, CDCl₃, 25 °C, TMS, δ ppm): 7.37-7.39 (m, 8H); 7.18-7.24 (m, 12H); 3.73 (d, *J* = 13.85 Hz, 4H); 3.33 (d, *J* = 13.85 Hz, 4H); 2.66-2.67 (m, 2H); 2.05-2.07 (m, 2H); 1.67-1.69 (m, 2H); 0.97-0.1.07 (m, 4H). ¹³C NMR (125 MHz, CDCl₃, 25 °C, TMS, δ ppm): 140.6, 128.9, 128.0, 58.2, 53.2, 25.9, 24.9. HR-MS: calculated value: 474.3035; found value [M⁺ + 1]: 475.2982.

² Arjan, H.; Boyd, E.; Coumbarides, G. S.; Eames, J.; Jones, R. V. H.; Stenson, R. A.; Suggate, M. J. *Tetrahedron Lett.* **2005**, *46*, 1921-1925.

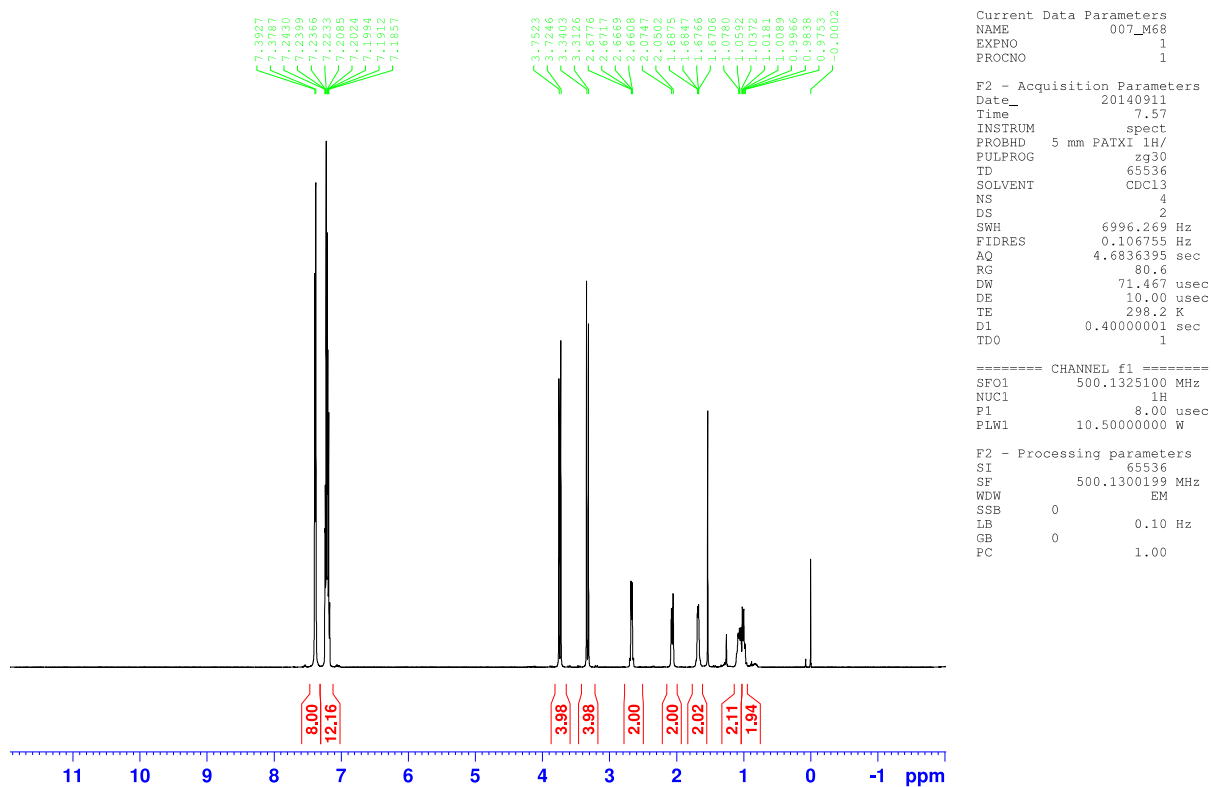


Figure S13: ^1H NMR spectrum of tetrabenzyl cyclohexyl-1,2-diamine **2a** in CDCl_3 at 25 °C

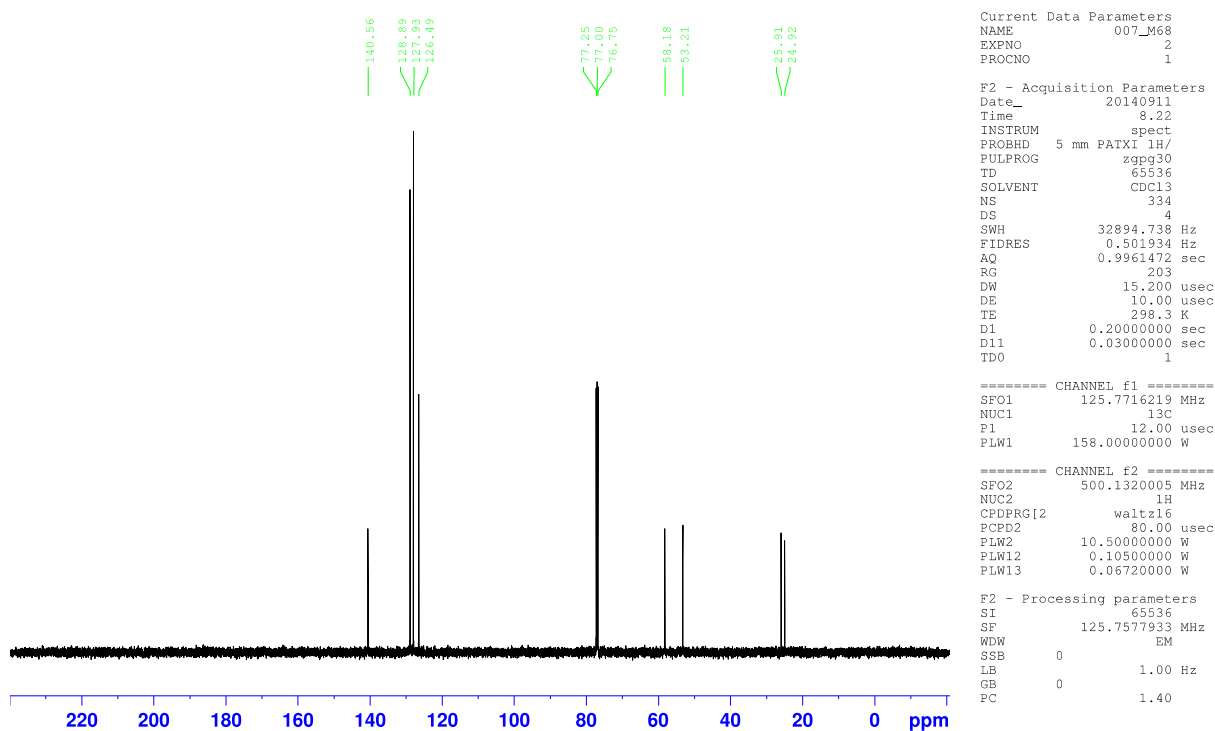
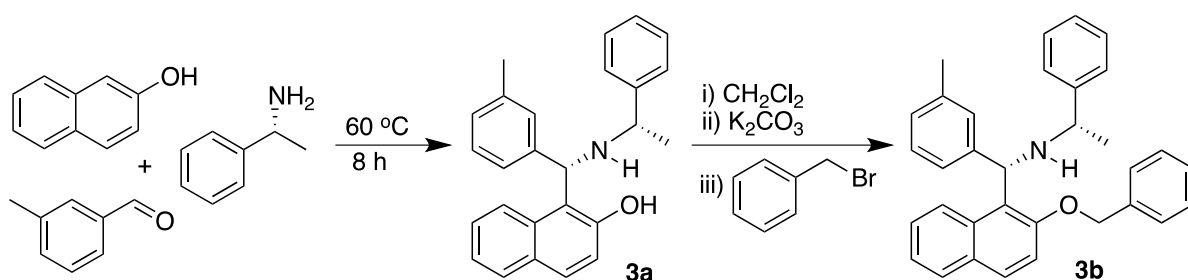


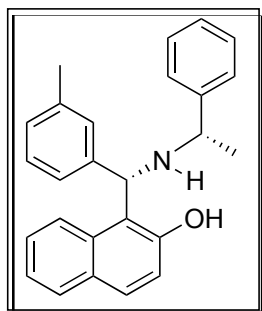
Figure S14: ^{13}C NMR spectrum of tetrabenzyl cyclohexyl-1,2-diamine **2a** in CDCl_3 at 25 °C

Typical procedure for the syntheses of 1,3-aminonaphthols



The 1,3 aminonaphthols **3** were synthesized and characterized as recently described.³ A mixture of 2-naphthol (2.0 mmol), aldehyde (2.4 mmol), and chiral amine (2.1 mmol) was stirred at 60 °C under nitrogen atmosphere. After stirring at reflux for 8 h (monitored by TLC), EtOH (5 mL) was added to the reaction mixture at room temperature. The crystals were collected, washed with EtOH (3 x 3 mL), and purified by crystallization from EtOAc/hexane to give the pure compounds.

Spectral data of compound **3a**:

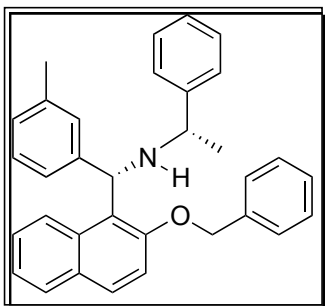


1-((S)-(((S)-1-phenylethyl)amino)(m-tolyl)methyl)naphthalen-2-ol

White crystals, 67 % yield. M.p. 170-171 °C. $[\alpha]_D^{20} + 197$ (c 1.00, CHCl₃). **¹H NMR** (500 MHz, CDCl₃, 25 °C, TMS, δ ppm): 13.73 (sbr, 1H); 7.69-7.72 (m, 2H); 7.32-7.39 (m, 4H); 7.15-7.22 (m, 5H); 7.10 (tap, $J = 7.8$ Hz, 1H); 6.96-6.97 (m, 3H); 5.40 (s, 1H); 3.87 (sbr, 1H); 2.21 (s, 3H); 1.47 (d, $J = 6.85$ Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃, 25 °C, TMS, δ ppm): 157.2; 143.1; 141.5; 138.7; 132.6; 129.6; 128.9; 128.7; 128.6; 128.5; 128.2; 127.8; 126.7; 126.3; 124.7; 122.3; 121.1; 120.0; 113.2; 60.3; 56.6; 22.9; 21.4. **IR (KBr)**: ν 3437, 3341, 3053, 2910, 2861, 1746, 1623, 1492, 1452, 1239, 916, 903, 857, 762, 621, 569, 538, 482 cm⁻¹. **HR-MS**: calculated value: 367.1936; found value $[M^+ + 1]$: 368.1982.

³ Dimitrov, V.; Shivachev, B.; Nikolova, R.; Chimov, A.; Kirilova, M. T.; Tzvetkova, P.; Kostova, K.; Marinova, M. *Tetrahedron: Asymmetry* **2013**, *24*, 1453-1466.

Spectral data of compound **3b**:



(S)-N-((S)-(2-(benzyloxy)naphthalen-1-yl)(m-tolyl)methyl)-1-phenylethanamine

Colorless crystals, 63 % yield. M.p. 110-111 °C. $[\alpha]_D^{20} + 53.3$ (c 1.00, CHCl₃). **¹H NMR** (500 MHz, CDCl₃, 25 °C, TMS, δ ppm): 7.76 (tap, $J = 6.70$ Hz, 2H); 7.13-7.37 (m, 15H); 7.06 (tap, $J = 7.55$, 1H); 7.00-7.02 (m, 2H); 6.94 (dap, $J = 7.35$ Hz, 1H); 5.63 (sbr, 1H); 5.03 (d, $J = 11.65$ Hz, 1H); 4.81 (d, $J = 11.65$ Hz, 1H); 3.60 (q, $J = 6.50$ Hz, 1H); 2.22 (s, 3H); 1.19 (d, $J = 6.55$ Hz, 3H); **¹³C NMR** (125 MHz, CDCl₃, 25 °C, TMS, δ ppm): 154.6, 146.4, 145.1, 137.4, 137.0, 129.1, 128.7, 128.6, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 127.6, 127.5, 127.4, 127.3, 126.8, 126.7, 126.5, 125.9, 124.0, 123.6, 115.0, 71.1, 55.8, 26.0, 21.7. **IR (KBr)**: ν 3437, 3341, 3028, 2969, 2861, 1959, 1866, 1807, 1746, 1384, 1329, 1310, 1168, 963, 934, 916, 903, 621, 569, 538, 522, 490, 437, 429 cm⁻¹. **HR-MS**: calculated value: 457.2406; found value [M + 1]: 458.2332.

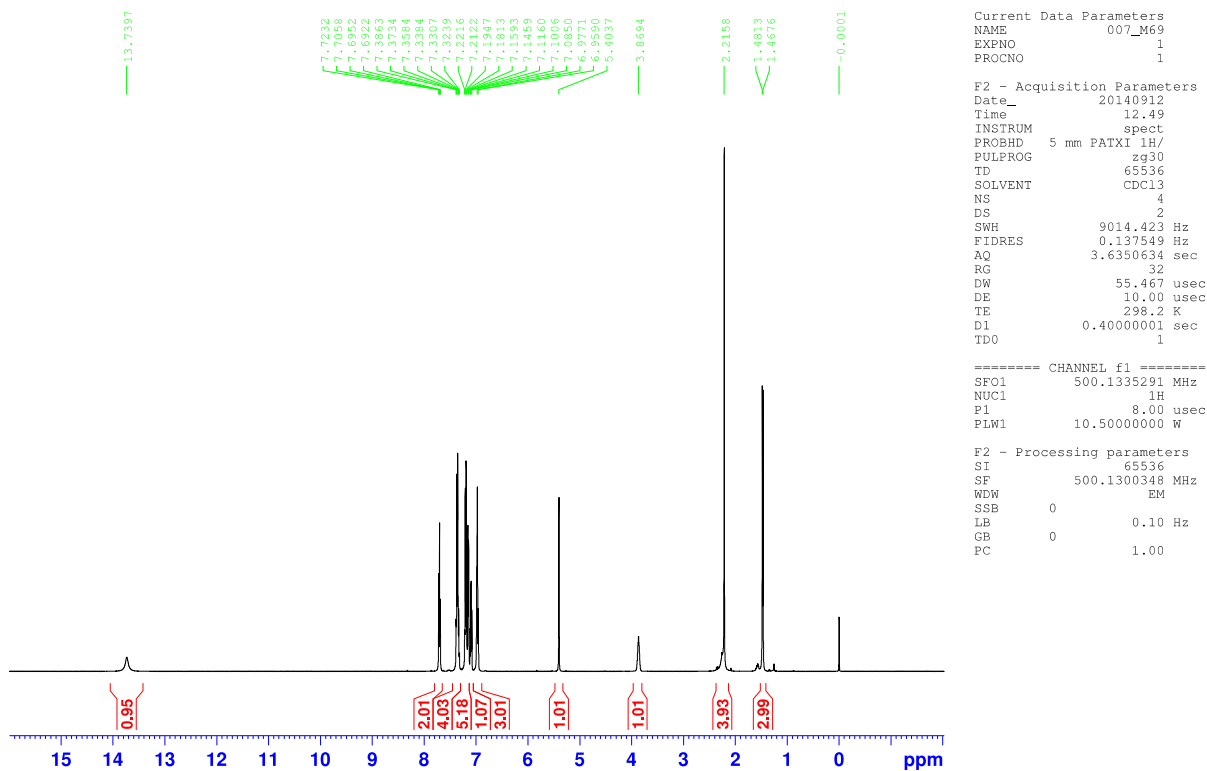


Figure S15: ^1H NMR spectrum of 1,3-aminonaphthol **3a** in CDCl_3 at 25 °C

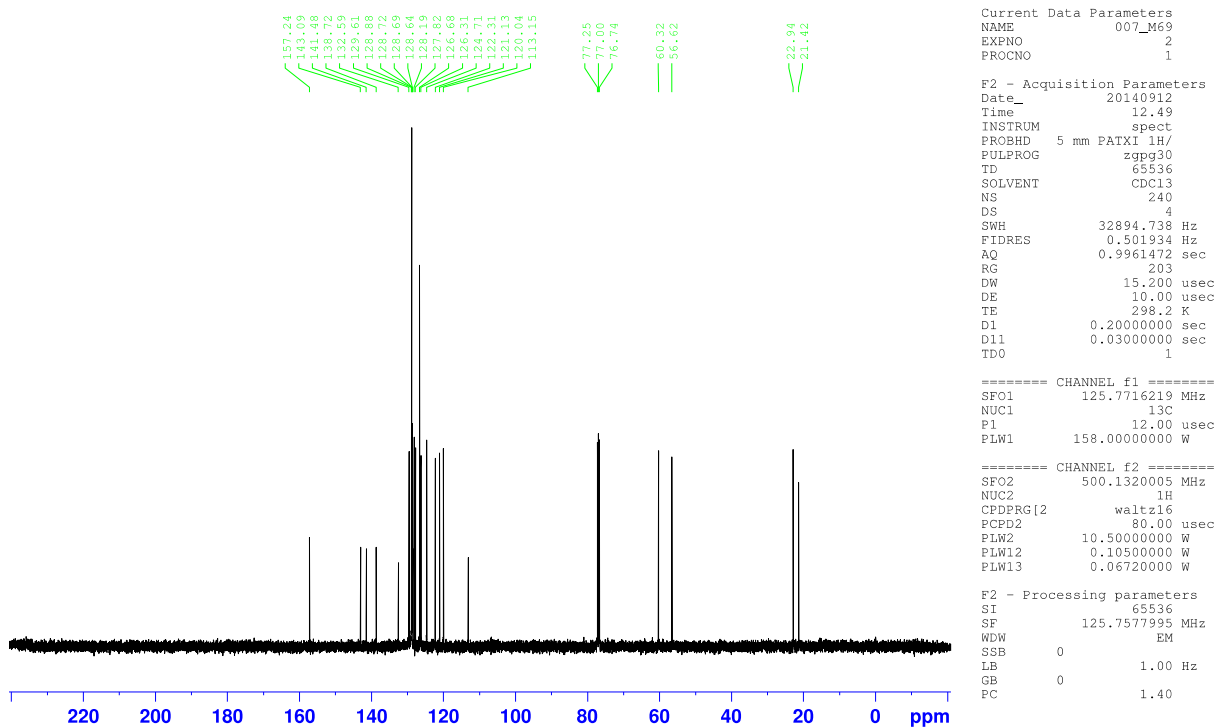


Figure S16: ^{13}C NMR spectrum of 1,3-aminonaphthol **3a** in CDCl_3 at 25 °C

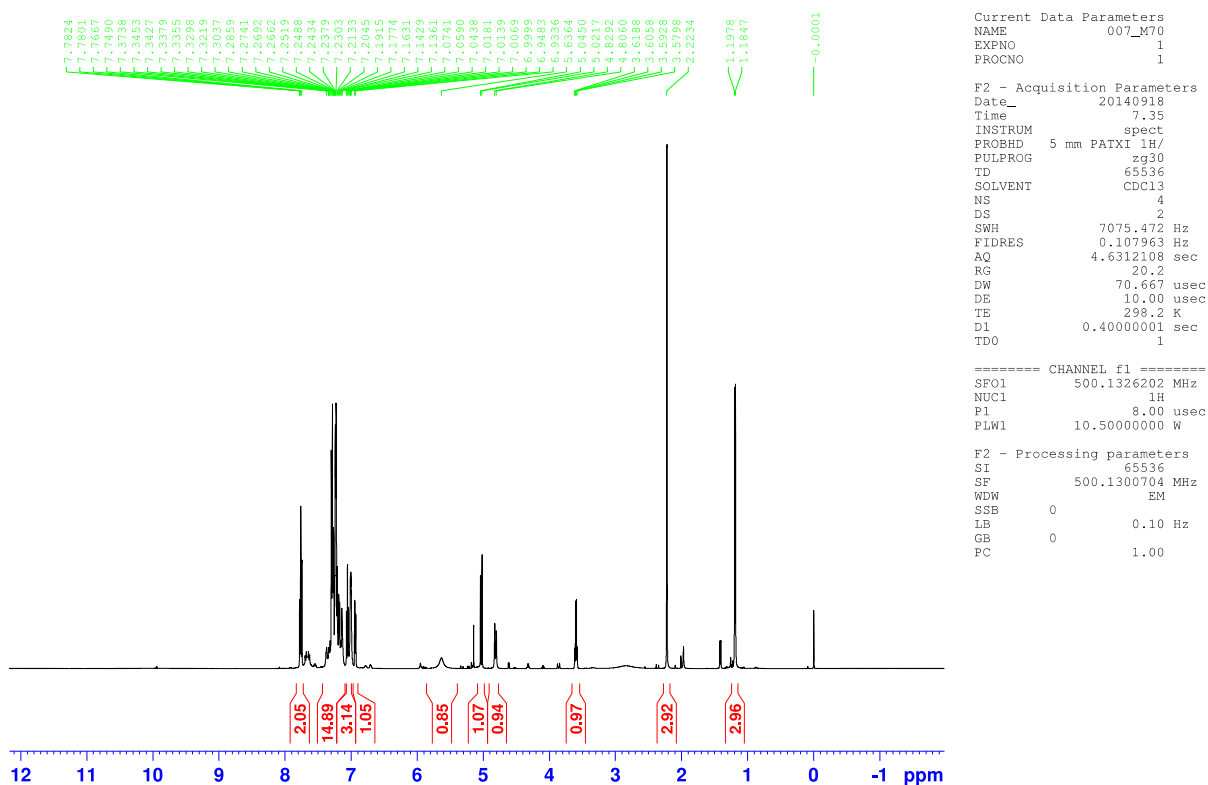


Figure S17: ^1H NMR spectrum of *O*-alkyl-1,3-aminonaphthol **3b** in CDCl_3 at 25 °C

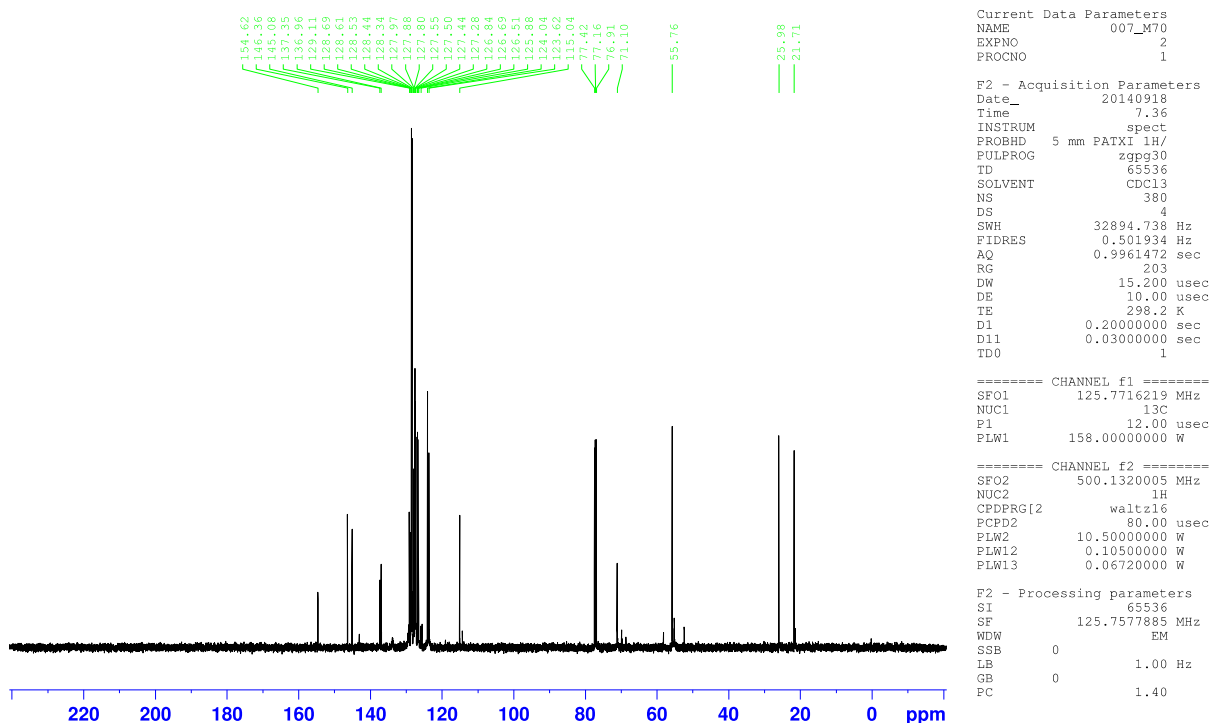


Figure S18: ^{13}C NMR spectrum of *O*-alkyl-1,3-aminonaphthol **3b** in CDCl_3 at 25 °C

Typical procedure for ^1H -NMR chiral discrimination

The ^1H NMR spectra were recorded at 500 MHz using 4 scans and 4.7 seconds of acquisition time at 25 °C probe temperature. For processing the NMR spectra was used 0.1 of line broadening and 64K of sized of fid. Samples for NMR spectroscopy were prepared by weighing and dissolving the appropriate amount of substrate in the respective deuterated solvent to prepare a 10 mM solution. The solutions were shaken for 2 minutes for equilibration time.

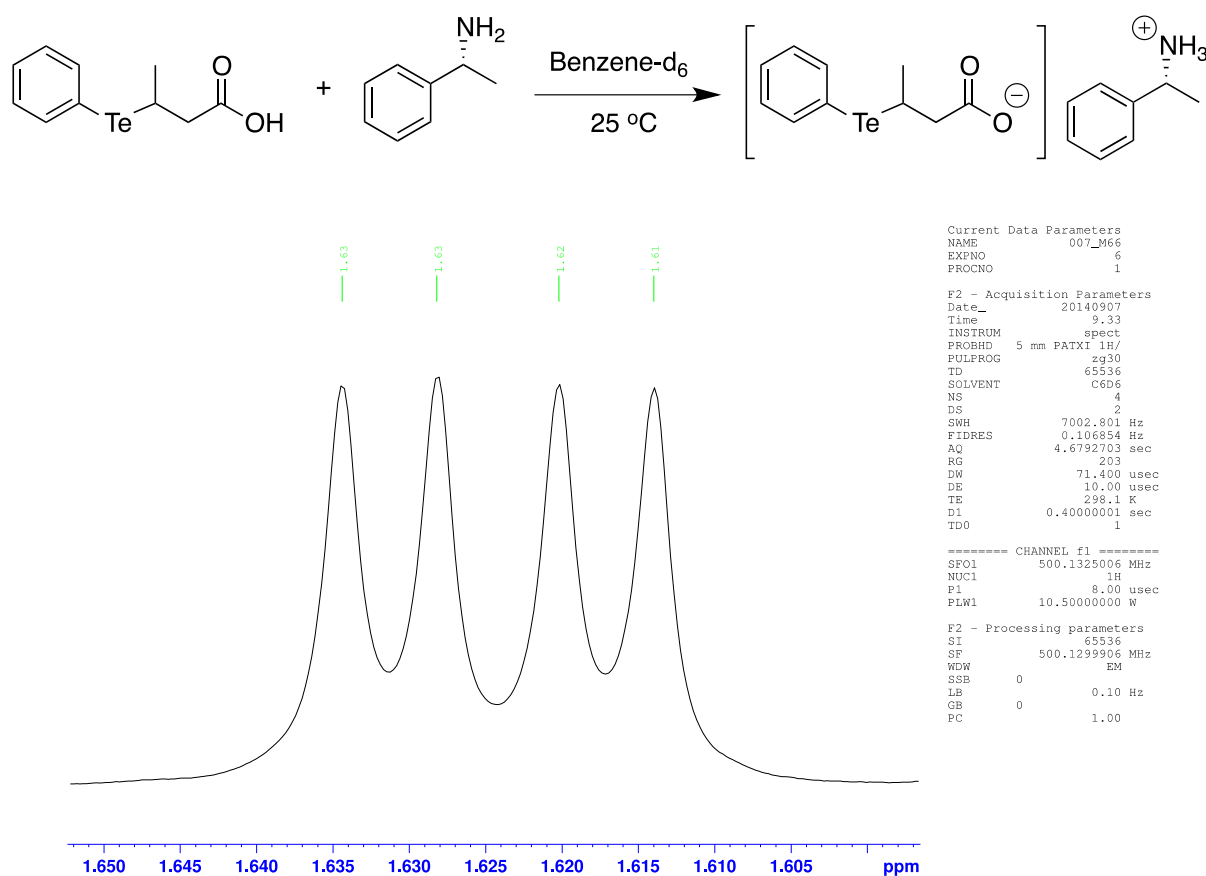


Figure S19: ^1H NMR spectrum for chiral discrimination of **1a** in benzene- d_6 at 25 °C

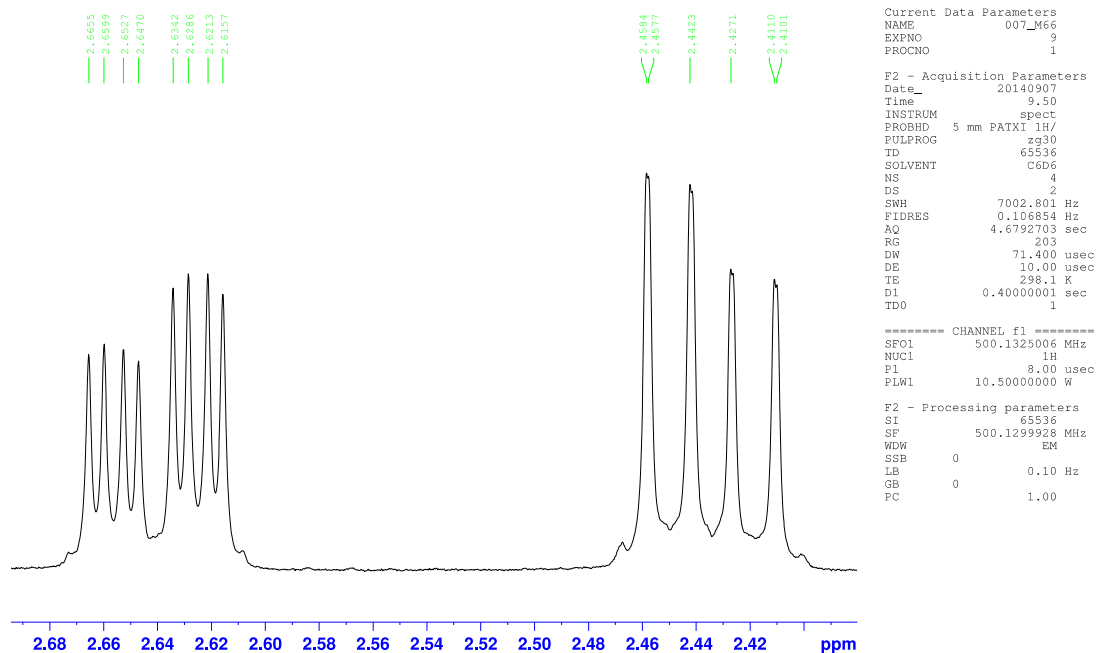
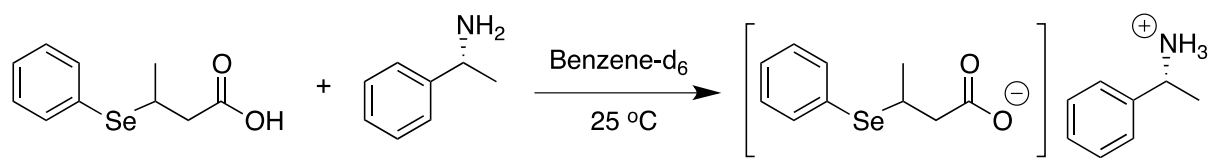


Figure S20: ^1H NMR spectrum for chiral discrimination of **1e** in Benzene- d_6 at 25 $^\circ\text{C}$

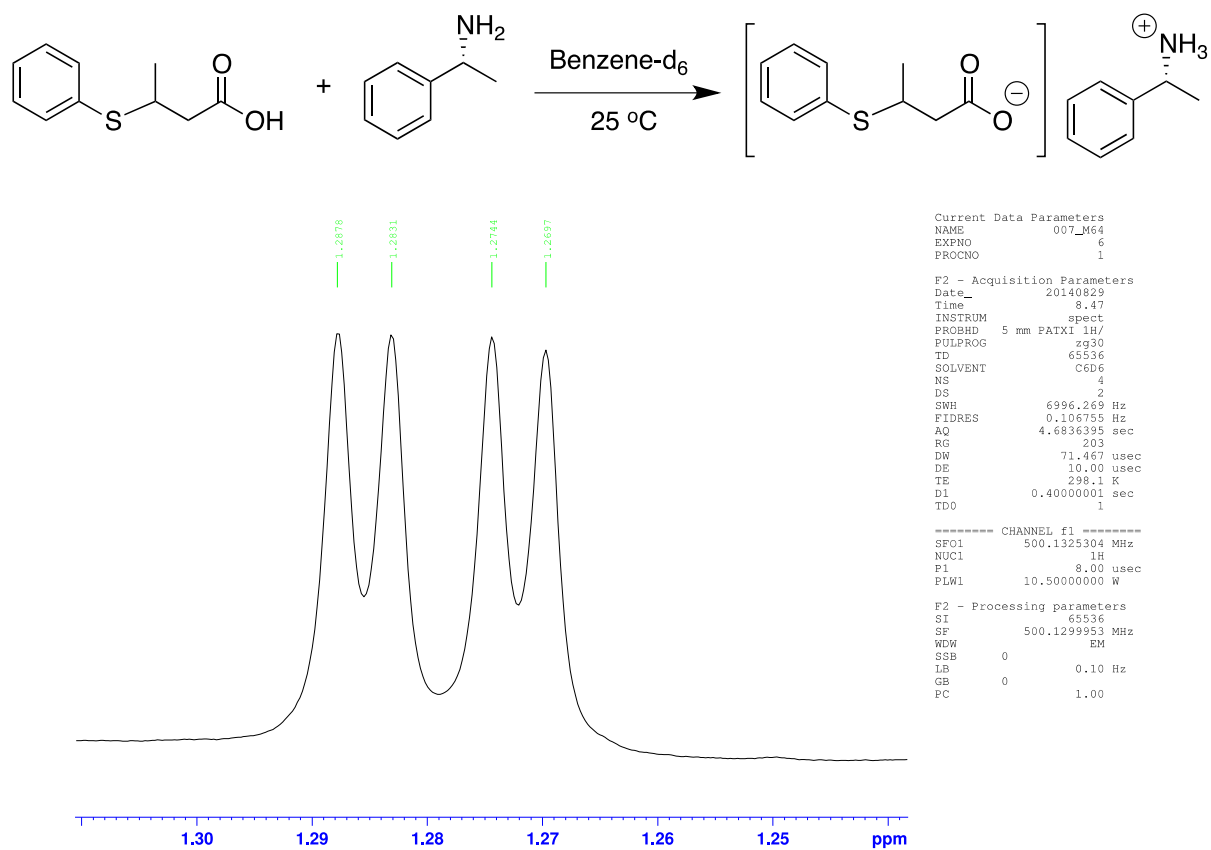


Figure S21: ^1H NMR spectrum for chiral discrimination of **1f** in Benzene- d_6 at 25 $^\circ\text{C}$

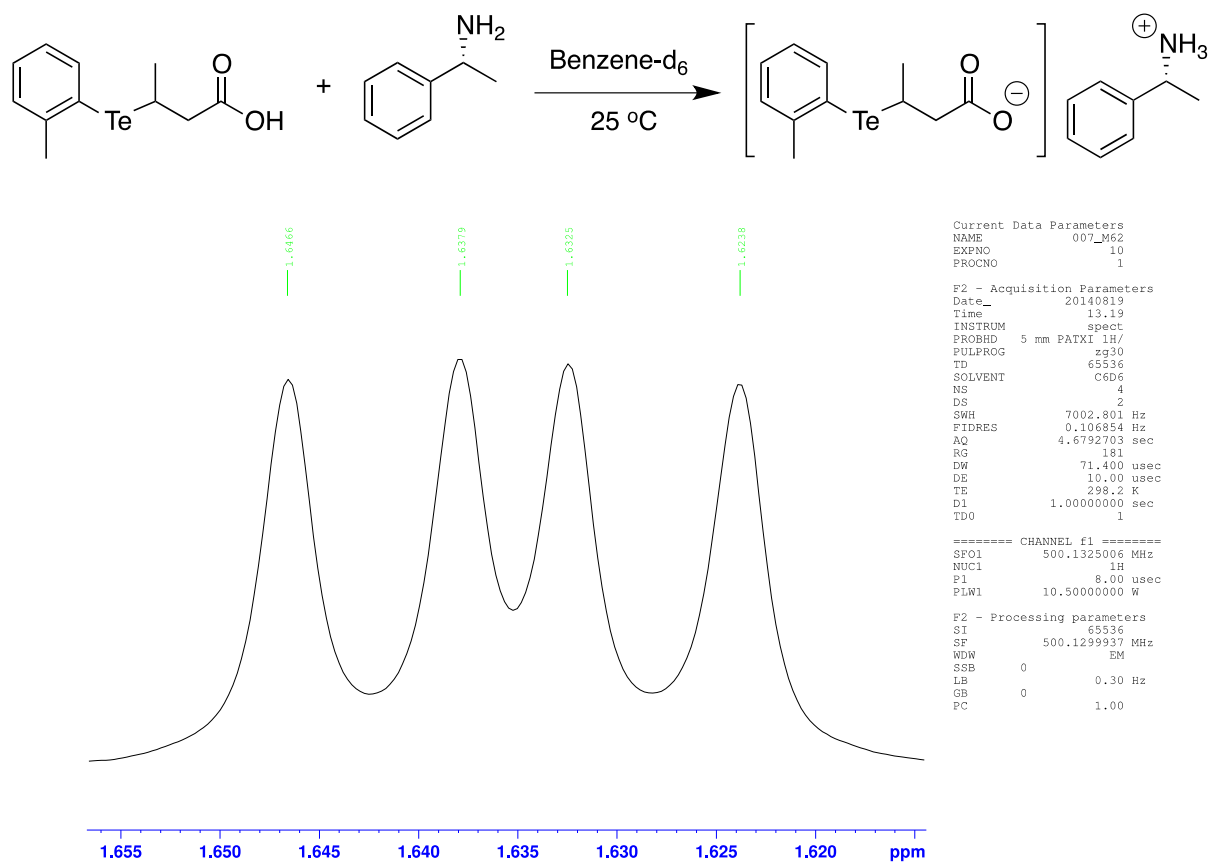


Figure S22: ^1H NMR spectrum for chiral discrimination of **1b** in Benzene- d_6 at 25 $^\circ\text{C}$

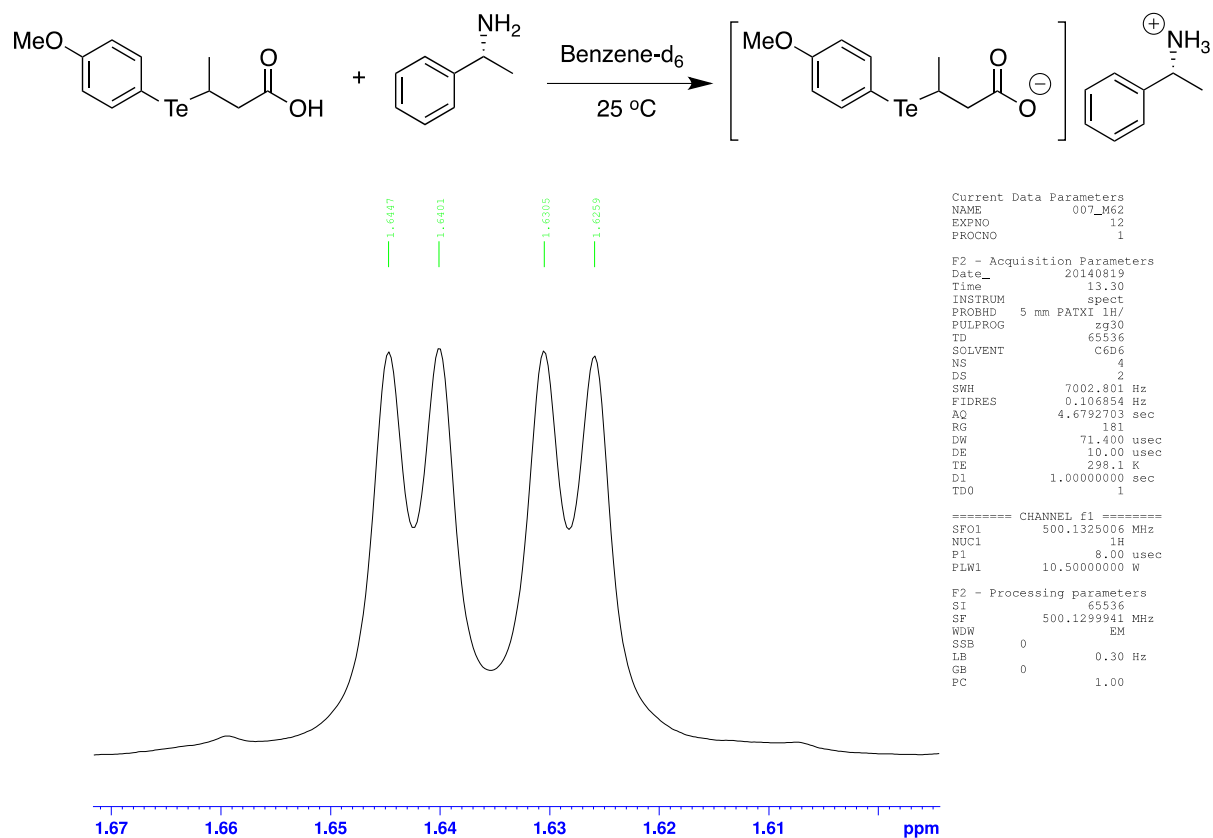


Figure S23: ^1H NMR spectrum for chiral discrimination of **1c** in Benzene- d_6 at $25\text{ }^\circ\text{C}$

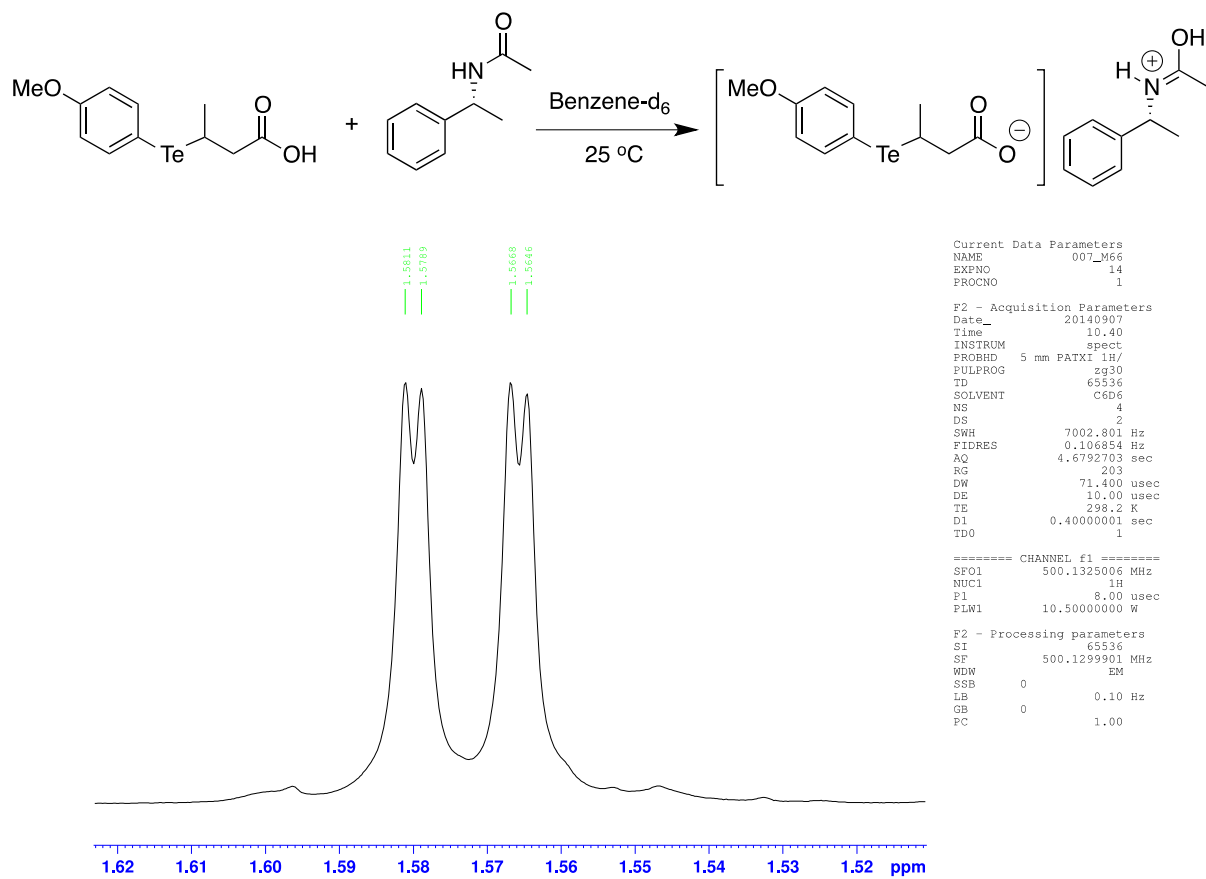


Figure S24: ^1H NMR spectrum for chiral discrimination of **1c** in Benzene- d_6 at 25 $^\circ\text{C}$

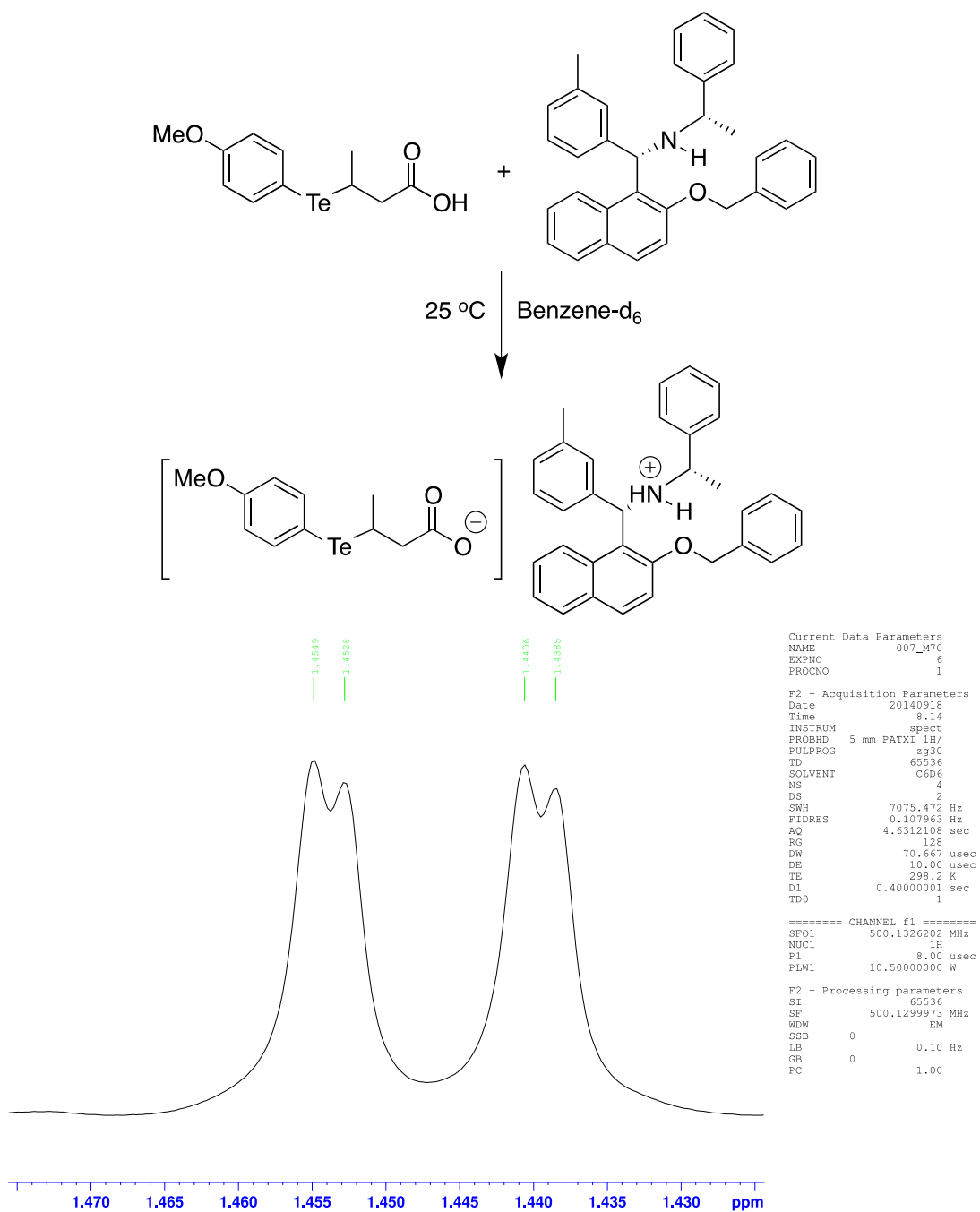


Figure S25: ¹H NMR spectrum for chiral discrimination of **1c** in Benzene-d₆ at 25 °C

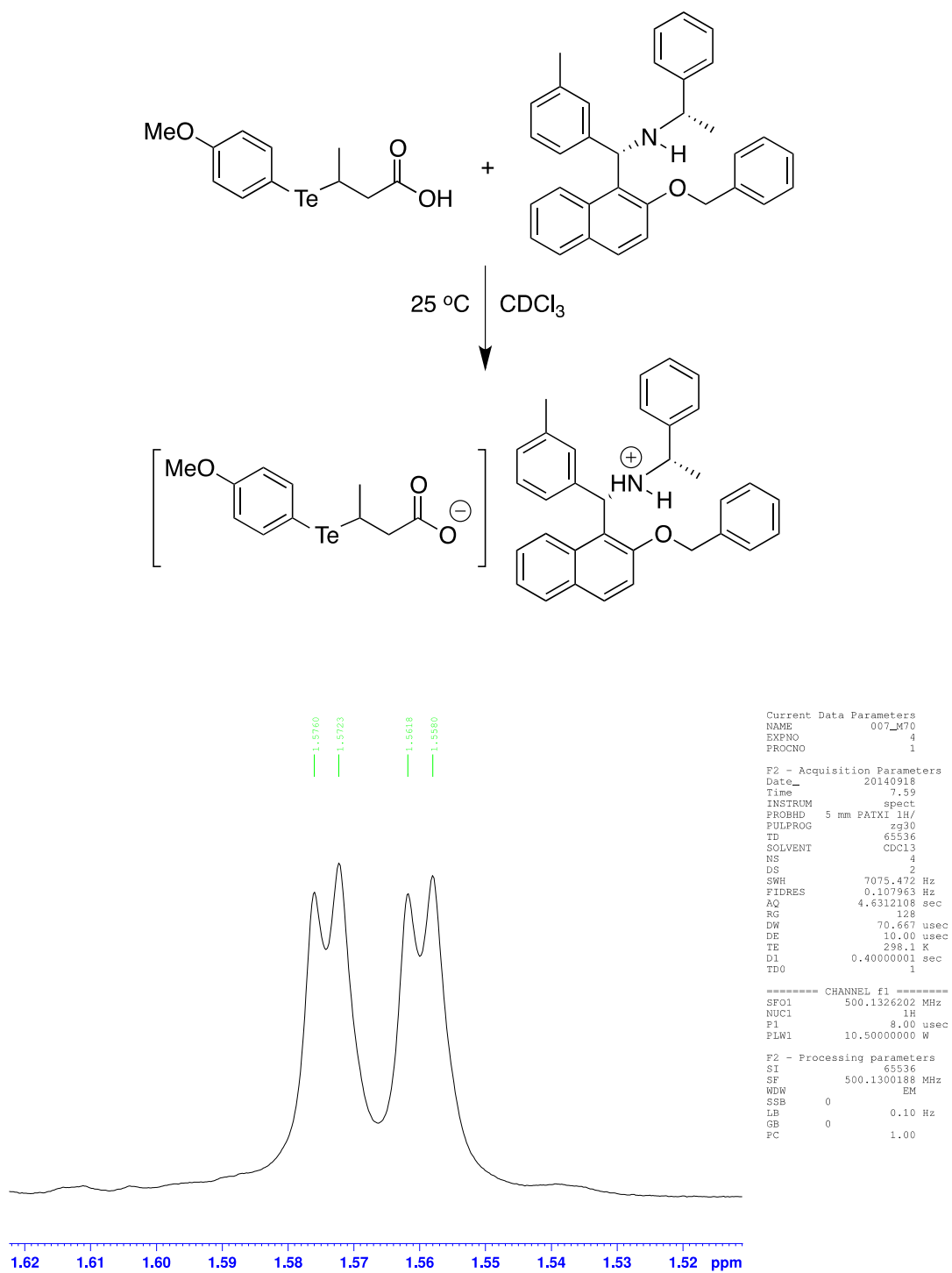


Figure S26: ¹H NMR spectrum for chiral discrimination of **1c** in CDCl₃ at 25 °C

Table S1: ¹H NMR chiral discrimination of organotellurocarboxylic acid **1c** with aminonaphthols **3a** and **3b**.^a

Entry	CSA	Solvent	Signal	$\Delta\delta$ [ppm]	$\Delta\Delta\delta$ [ppm]	$\Delta\Delta\delta$ [Hz]
1	3a	CDCl ₃	----	----	----	----
2	3a	Benzene-d ₆	----	----	----	----
3	3a	DMSO-d ₆	----	----	----	----
4	3b	Benzene-d ₆	2	+ 0.030	0.0021	1.05
5	3b	CDCl ₃	2	- 0.024	0.0037	1.85
6	3b	DMSO-d ₆	----	----	----	----

^a An equimolecular amount of aminonaphthol **3** and carboxylic acid **1c** were diluted in respective deuterated solvent (10 mM) at 25 °C.

the

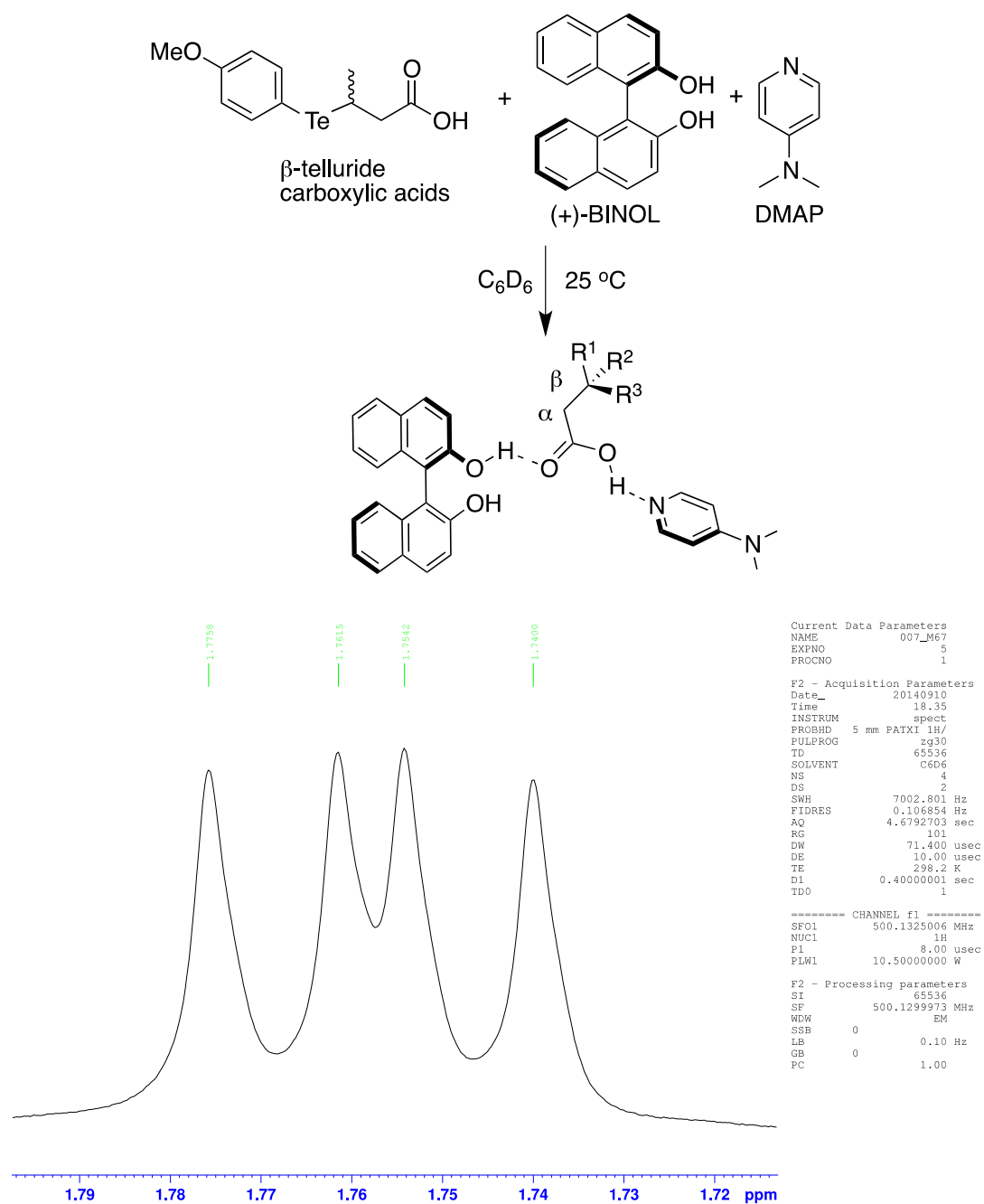


Figure S27: 1H NMR spectrum for chiral discrimination of **1c** in benzene- d_6 at 25 °C

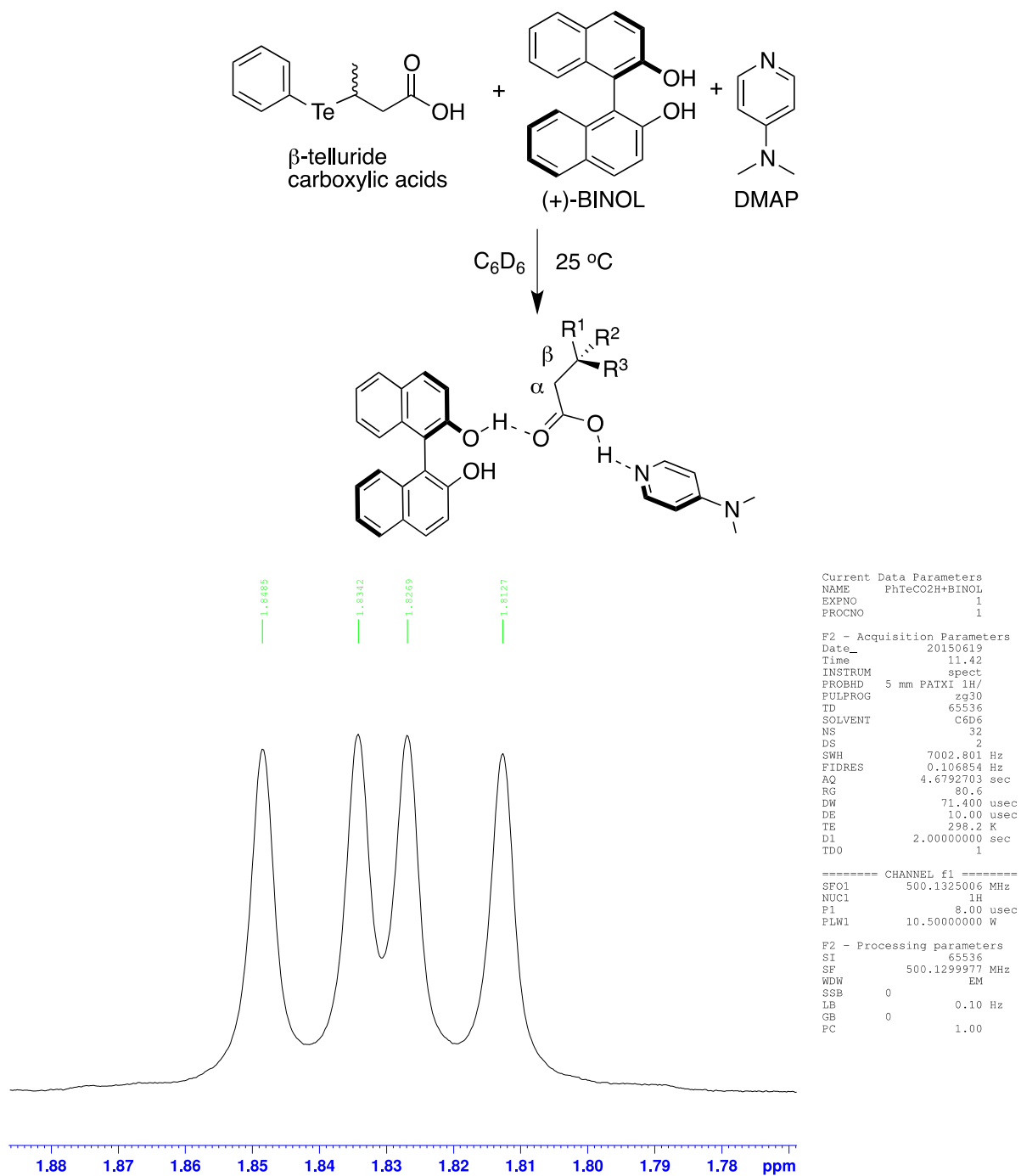


Figure S28: 1H NMR spectrum for chiral discrimination of **1a** in benzene- d_6 at 25 °C

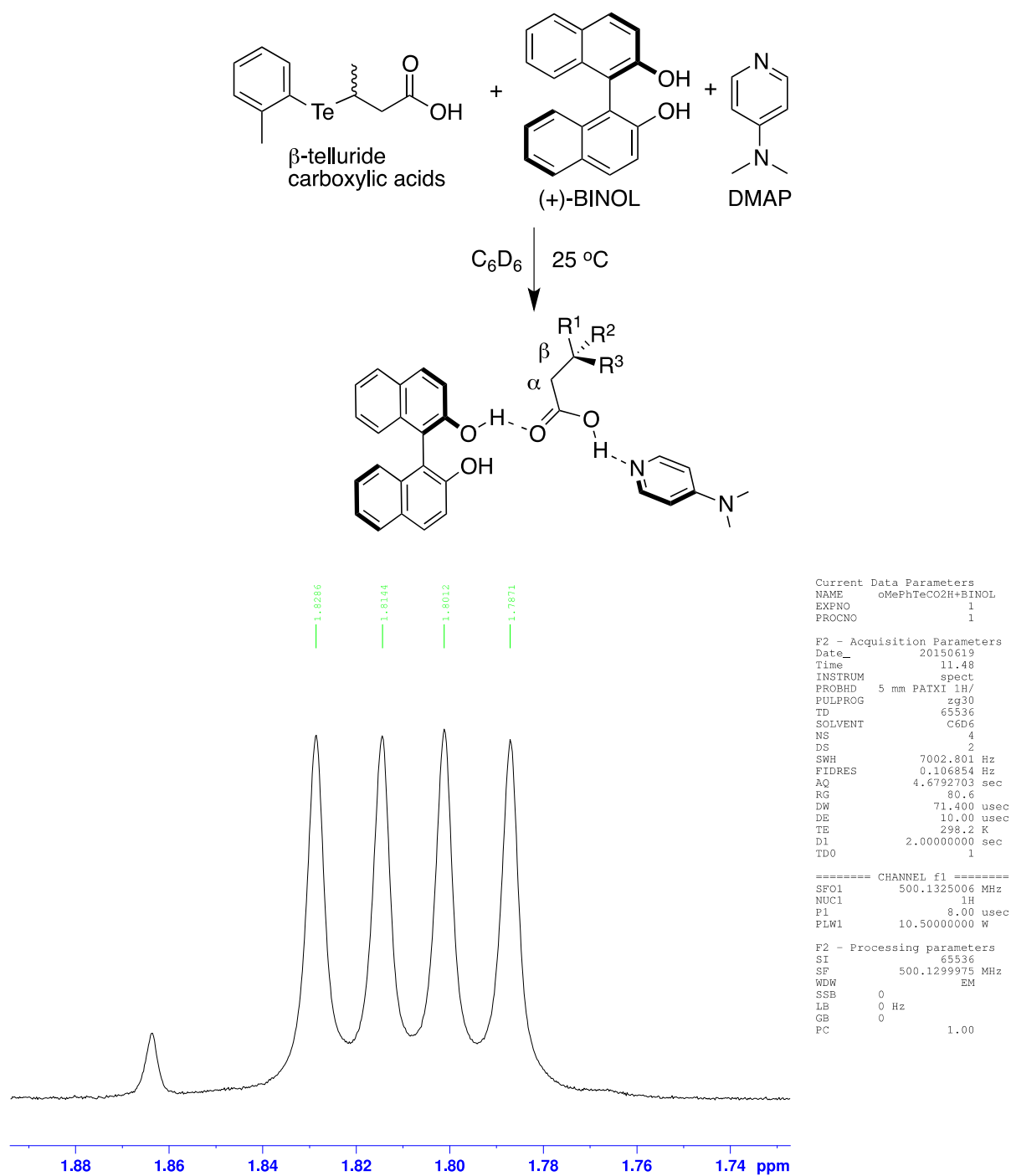


Figure S29: ^1H NMR spectrum for chiral discrimination of **1b** in benzene- d_6 at 25 °C

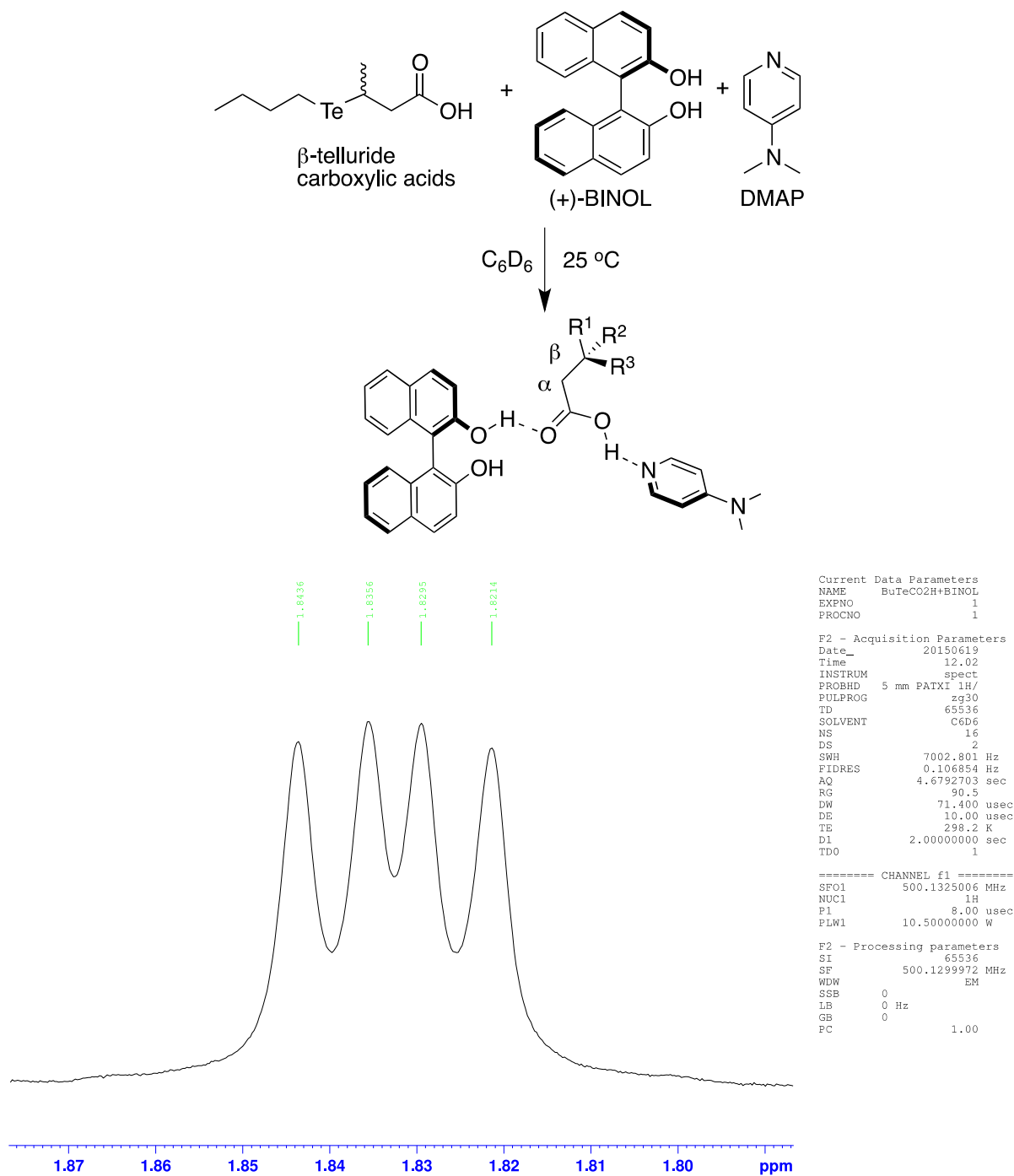


Figure S30: ^1H NMR spectrum for chiral discrimination of **1d** in benzene- d_6 at 25 $^\circ\text{C}$

Typical procedure for ^{125}Te -NMR chiral discrimination

The ^{125}Te NMR spectra were recorded at 94.79 MHz using 128 scans and 0.087 seconds of acquisition time at 25 °C probe temperature. For processing the NMR spectra was used 3.0 of line broadening and 64K of sized of fid. Samples for NMR spectroscopy were prepared by weighing and dissolving the appropriate amount of substrate in the respective deuterated solvent to prepare a 20 mM solution. The solutions were shaken for 2 minutes for equilibration time.

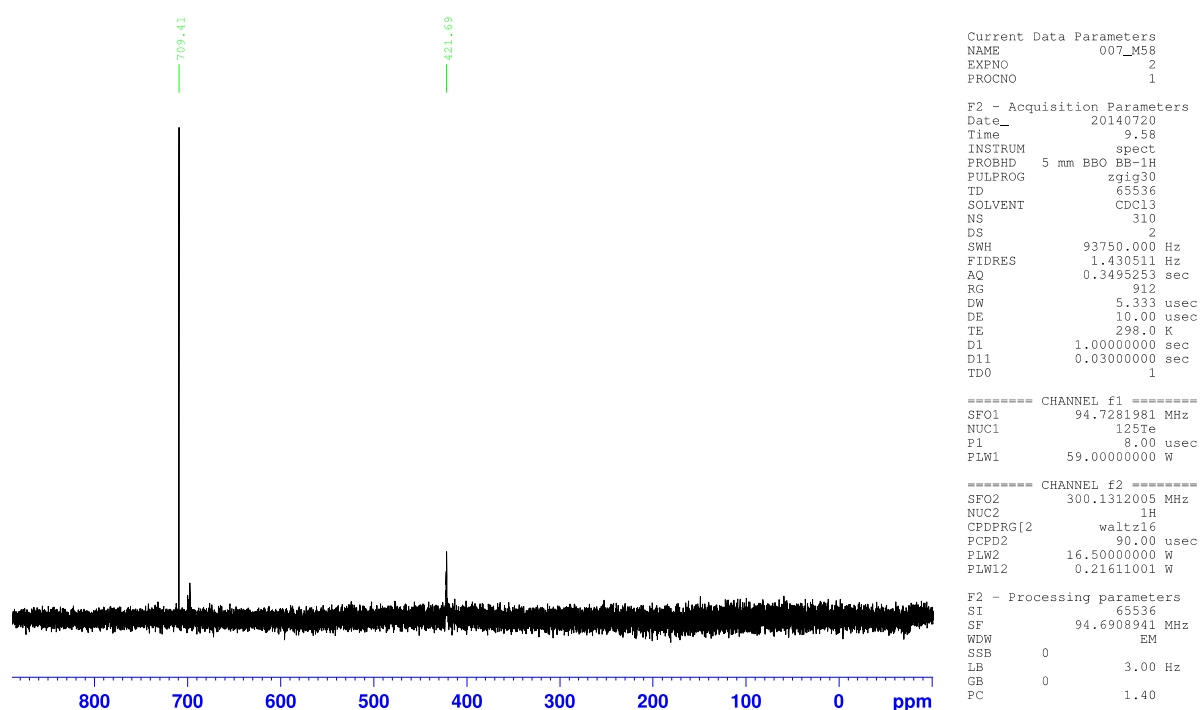


Figure S31: ^{125}Te NMR spectrum of organochalcogenide **1a** in CDCl_3 at 25 °C

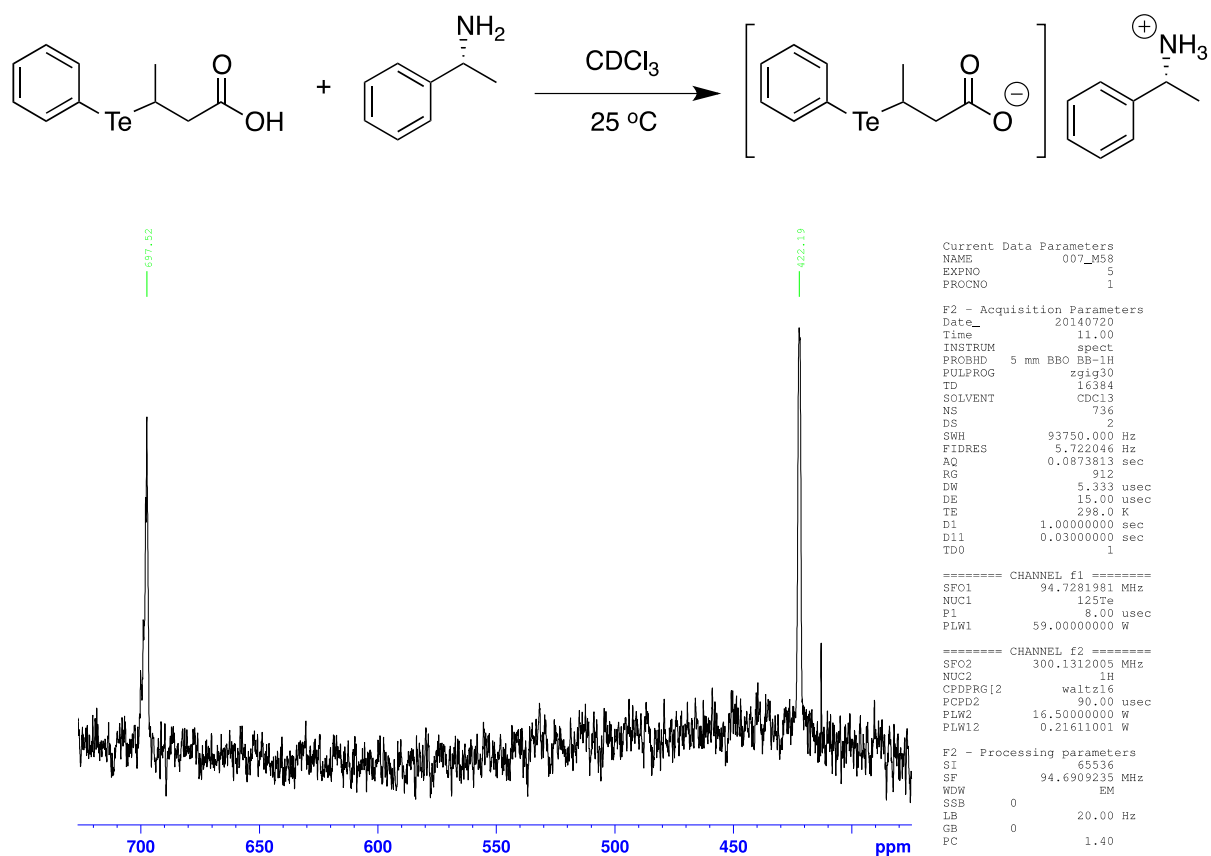


Figure S32: ^{125}Te NMR spectrum for chiral discrimination of **1a** with 0.8 equiv. of chiral probe in CDCl_3 at 25 $^\circ\text{C}$

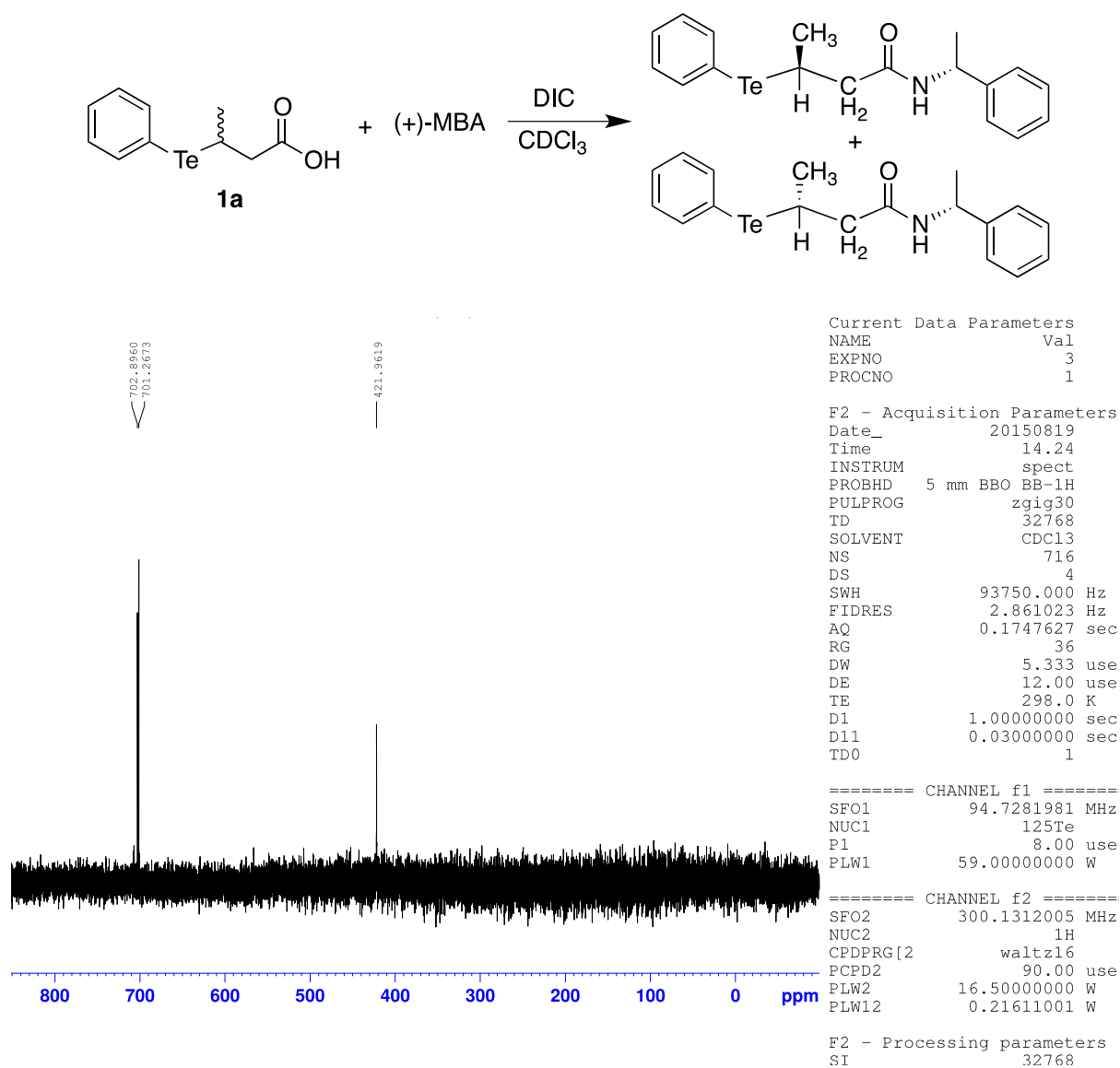


Figure S33: ^{125}Te NMR spectrum for chiral discrimination of **1a** by reaction with (+)-MBA and DIC in CDCl_3 at 25°C .

Deconvolution of diastereomers peaks of ^1H NMR spectrum

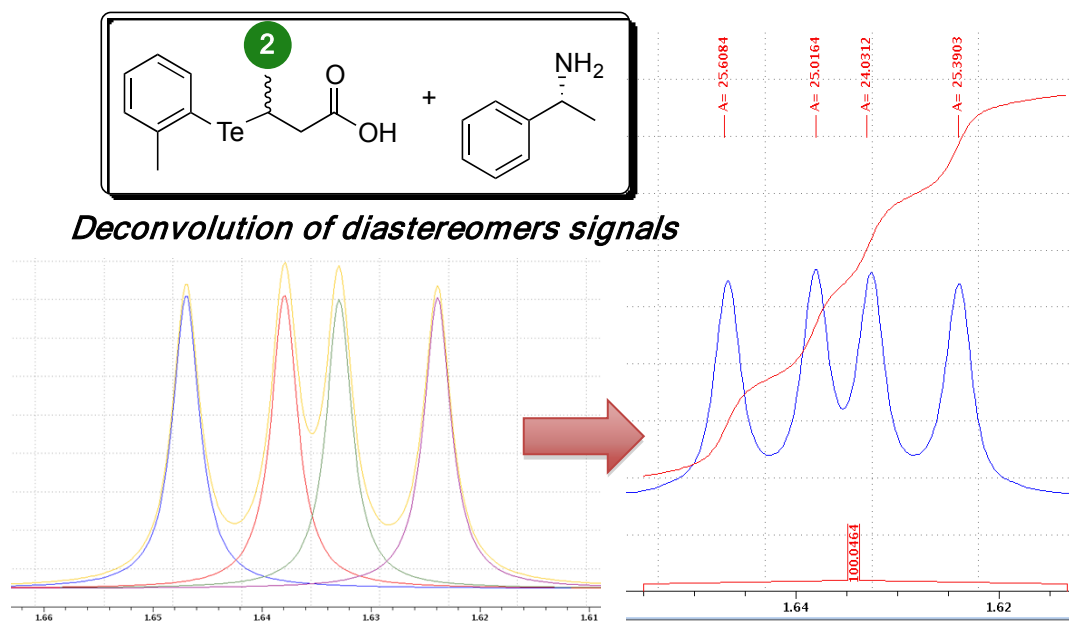


Figure S34: Deconvolution of diastereomers peaks of ^1H NMR spectrum for chiral discrimination of **1b** in Benzene- d_6 at 25 $^\circ\text{C}$.