

Supporting Information

Catalytic asymmetric cycloadditions between aldehydes and enolizable anhydrides: *cis*-selective dihydroisocoumarin formation with excellent enantiocontrol

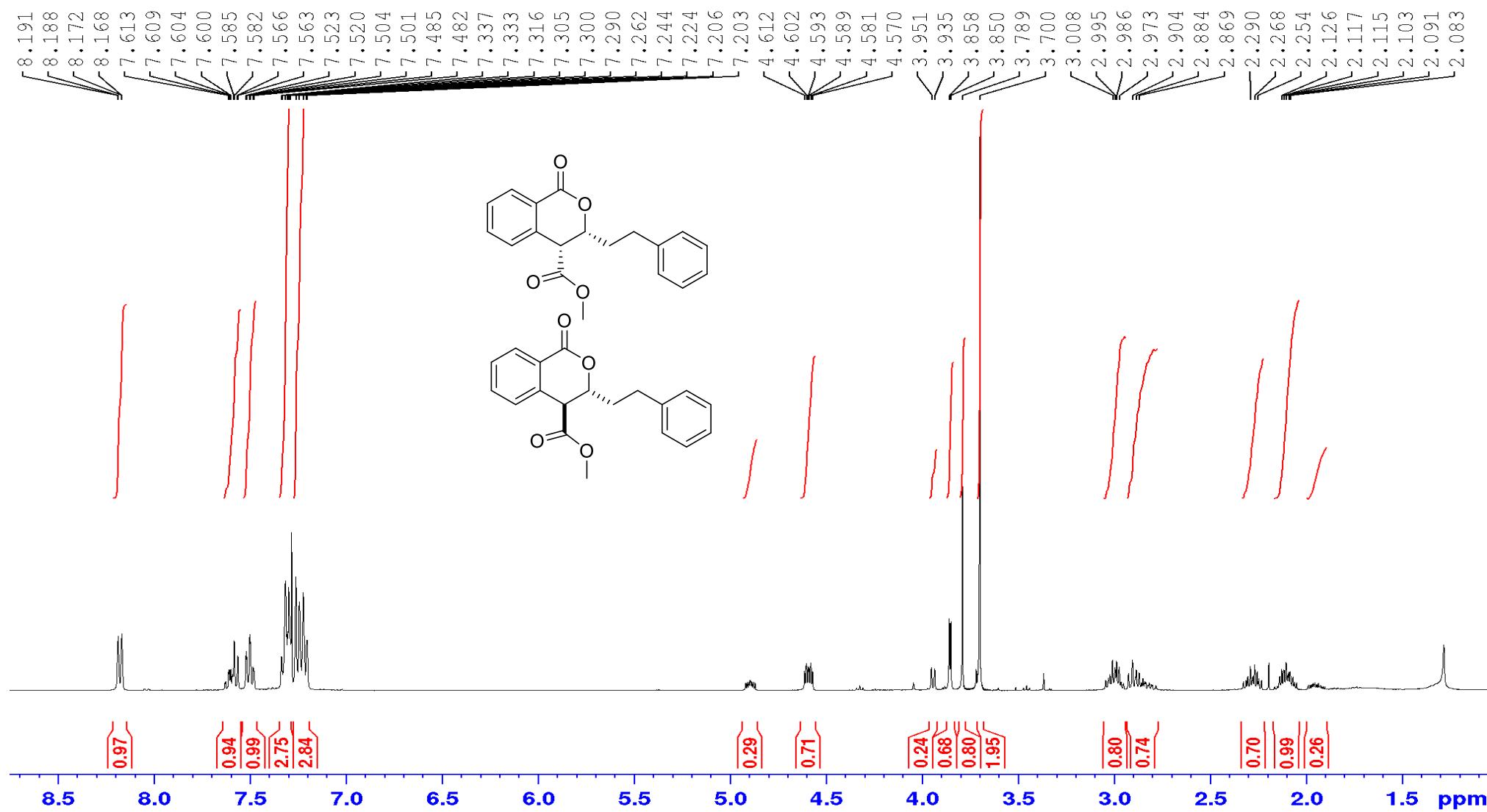
*Maria Luisa Aiello, Umar Farid, Cristina Trujillo, Brendan Twamley and Stephen J. Connolly**

Trinity Biomedical Sciences Institute, School of Chemistry, The University of Dublin, Trinity College, Dublin 2, Ireland

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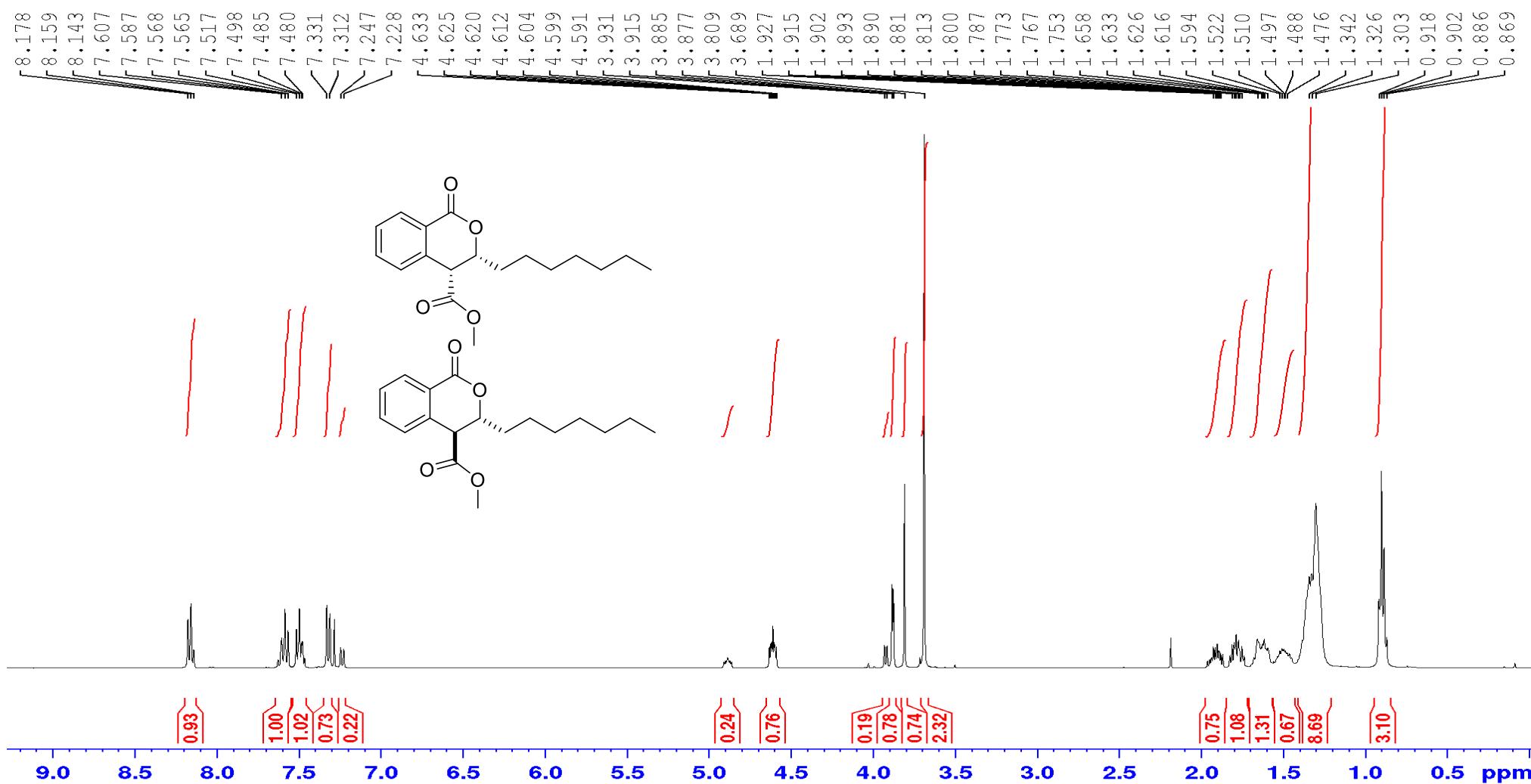
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1 NMR Spectra ^1H NMR (400 MHz, CDCl_3) spectra of *cis*-15 and *trans*-15



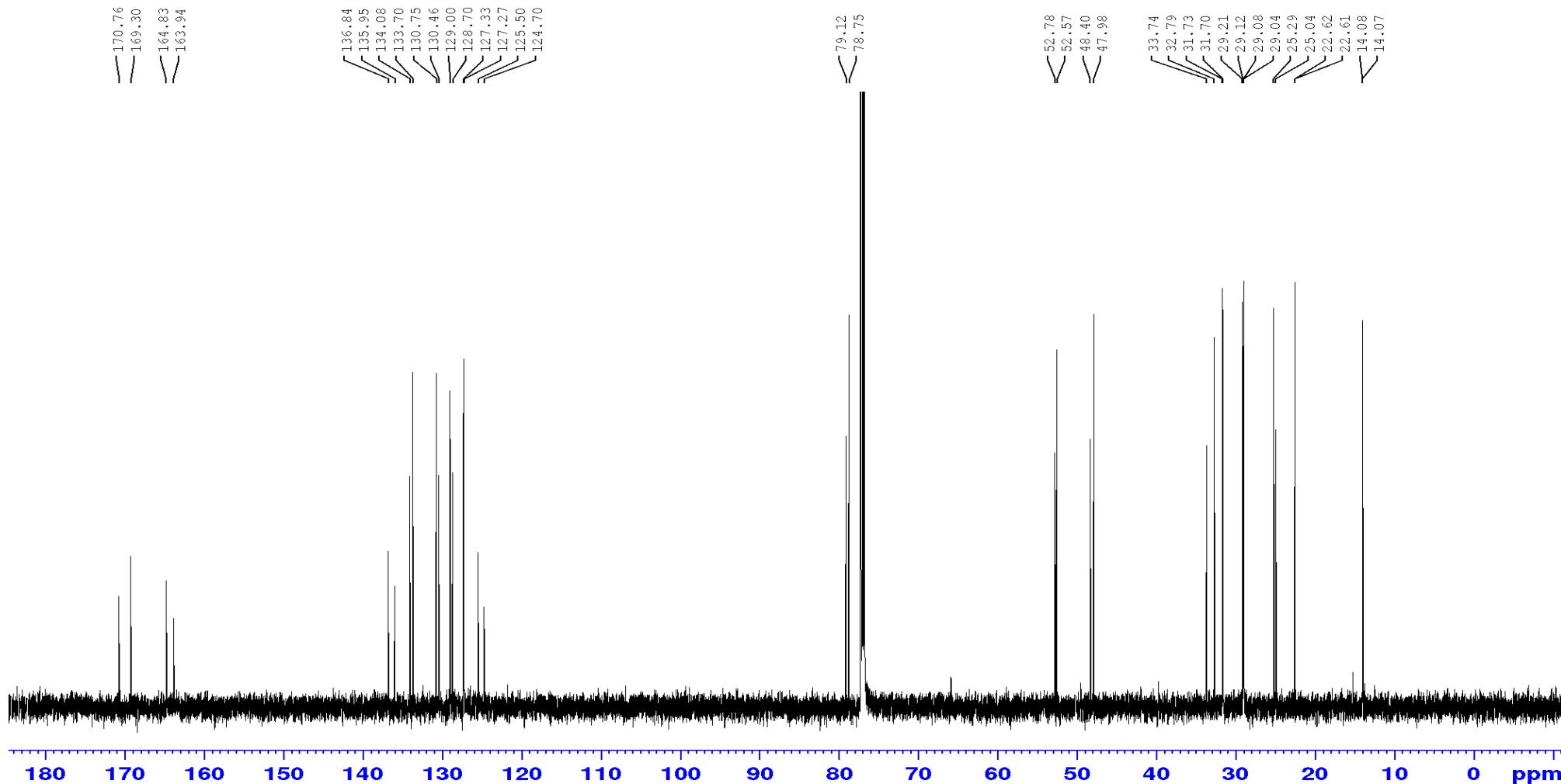
S2

¹H NMR (400 MHz, CDCl₃) spectra of *cis*-31 and *trans*-31

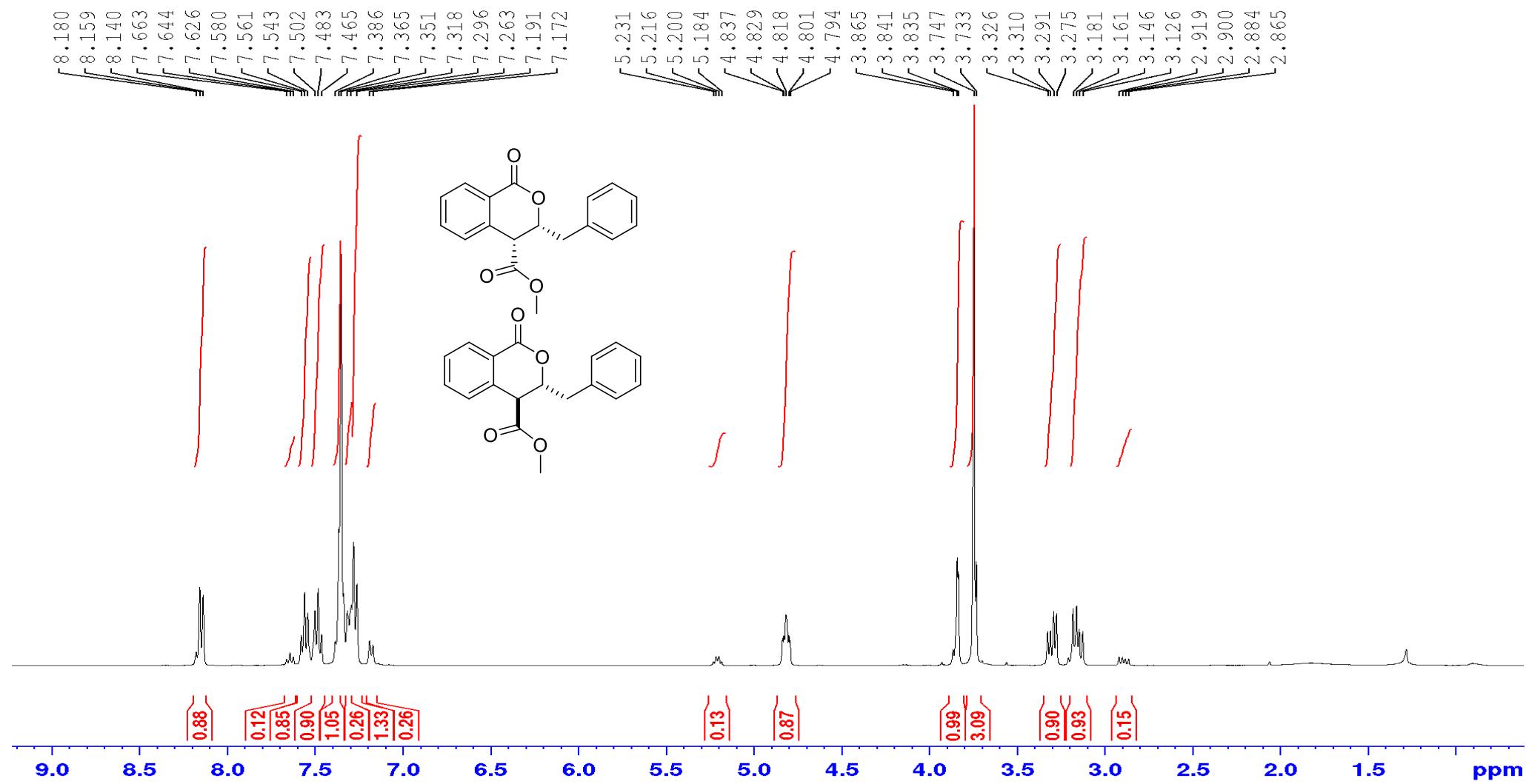


S3

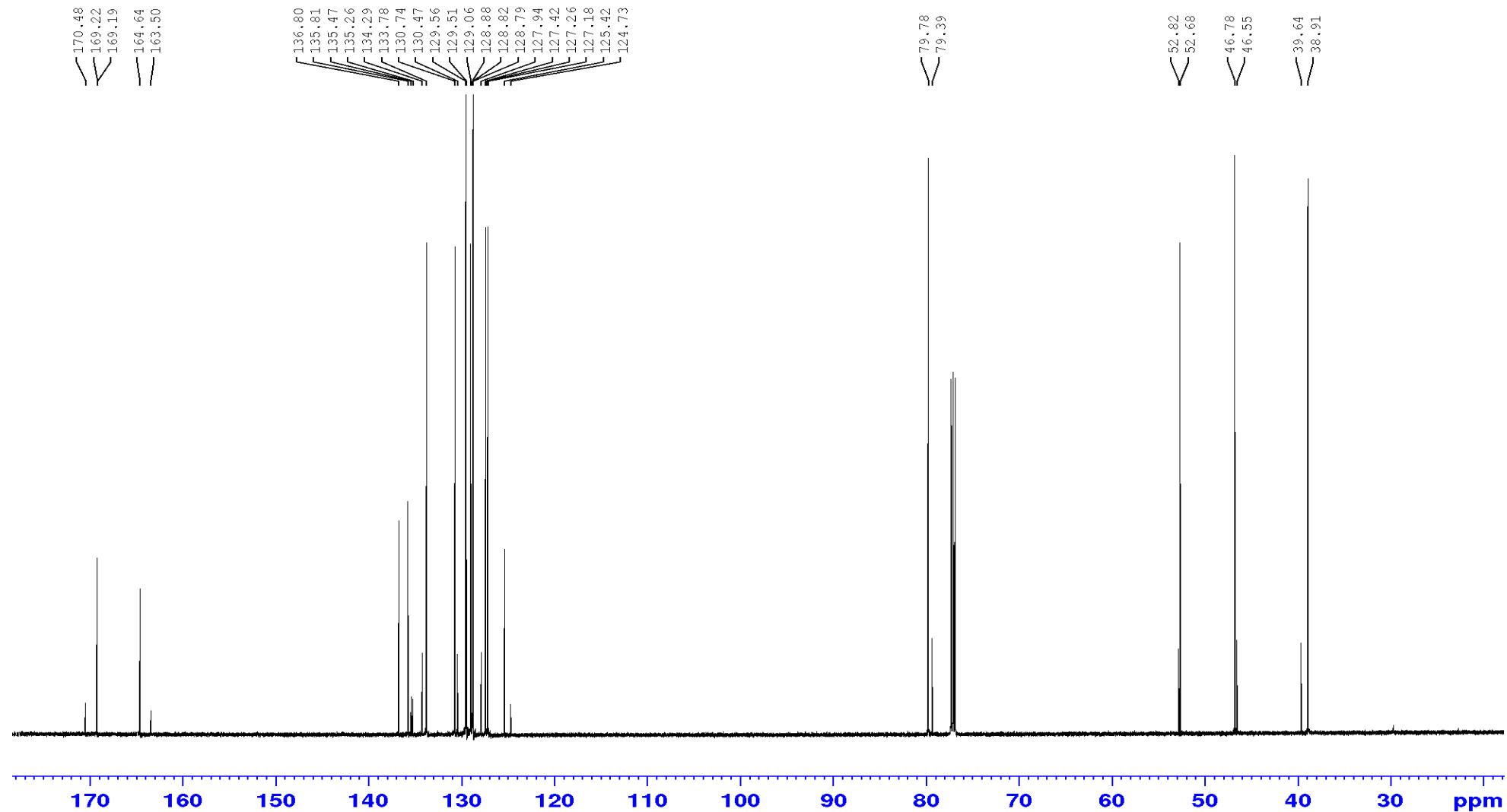
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-31 and *trans*-31



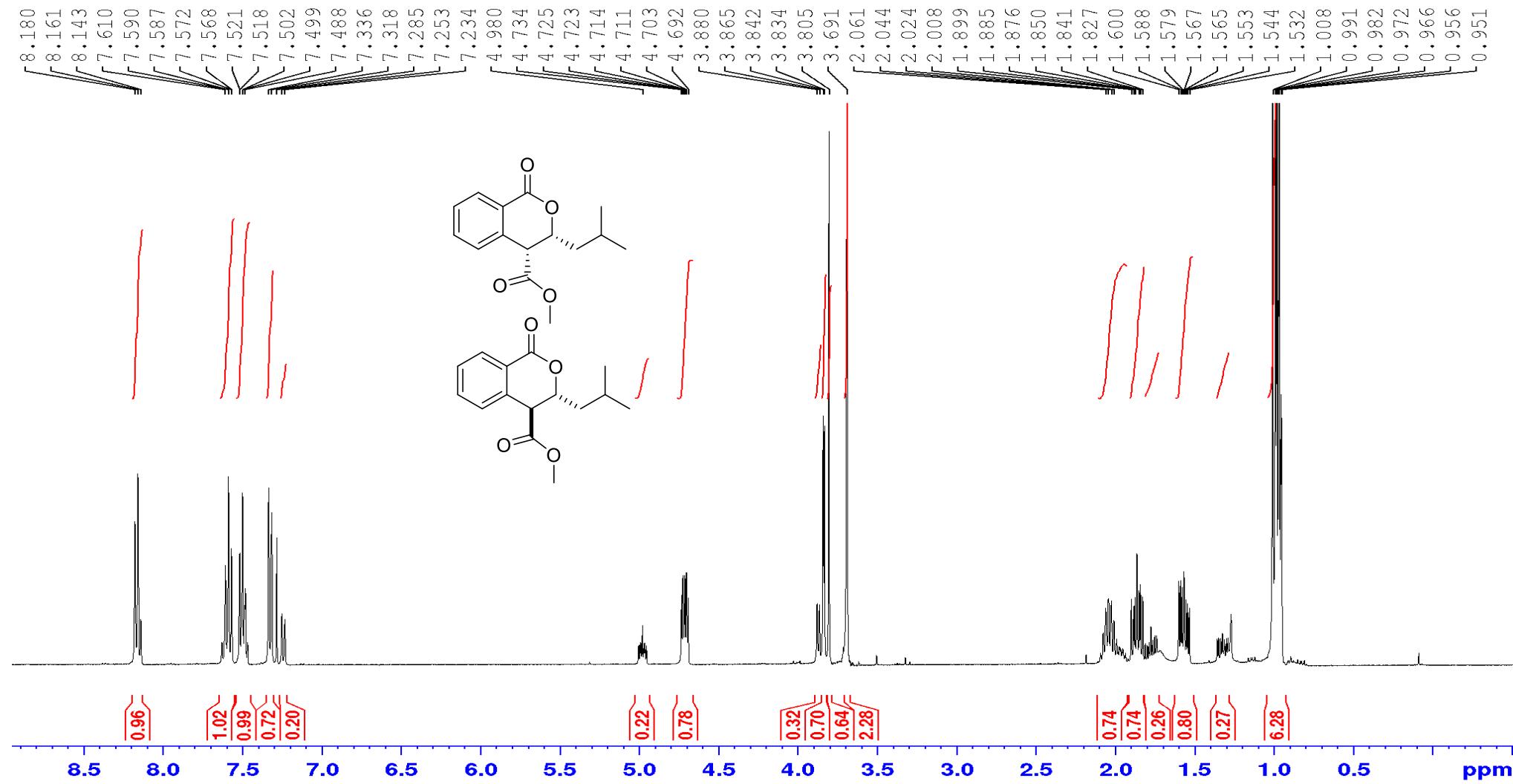
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-32 and *trans*-32



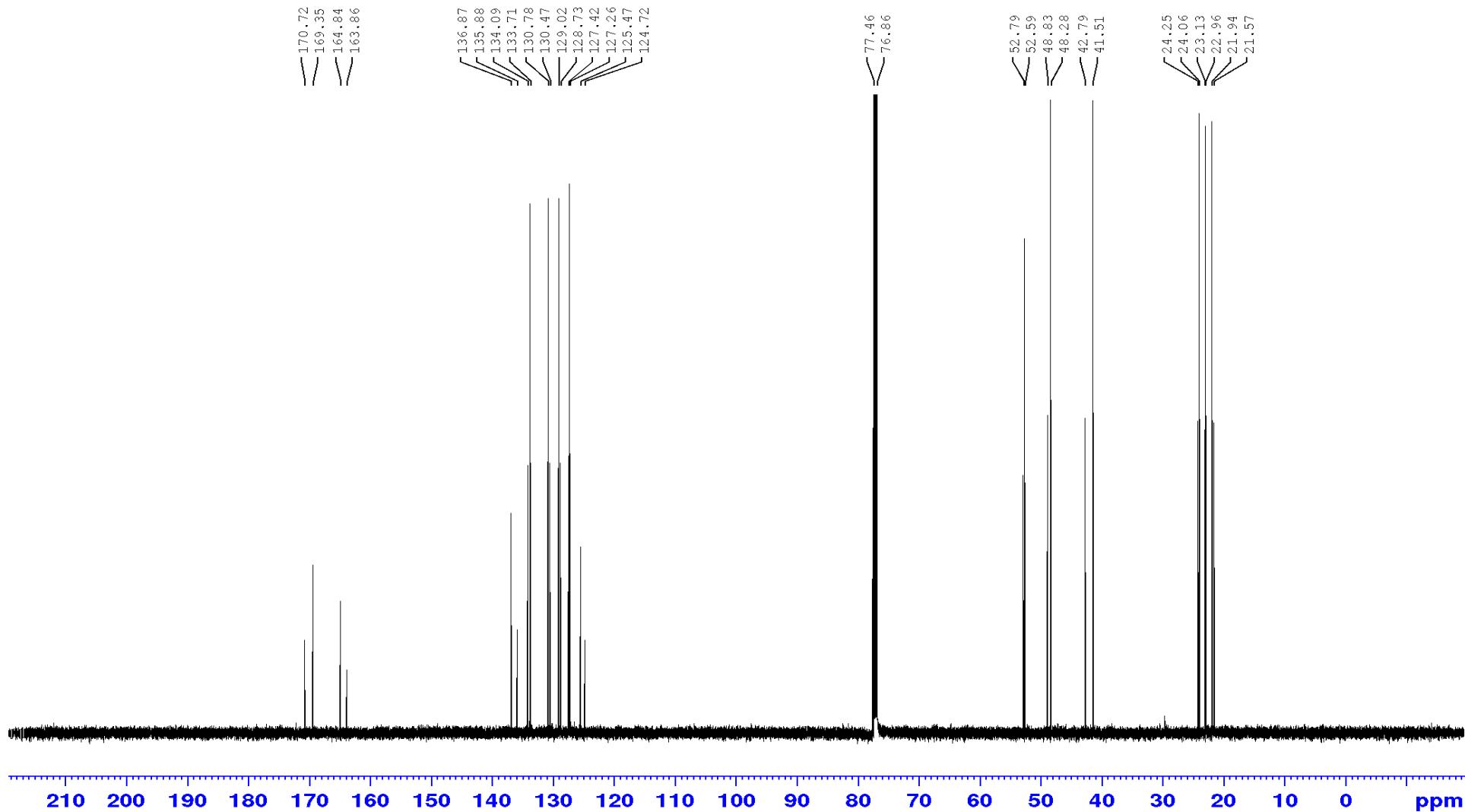
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-32 and *trans*-32



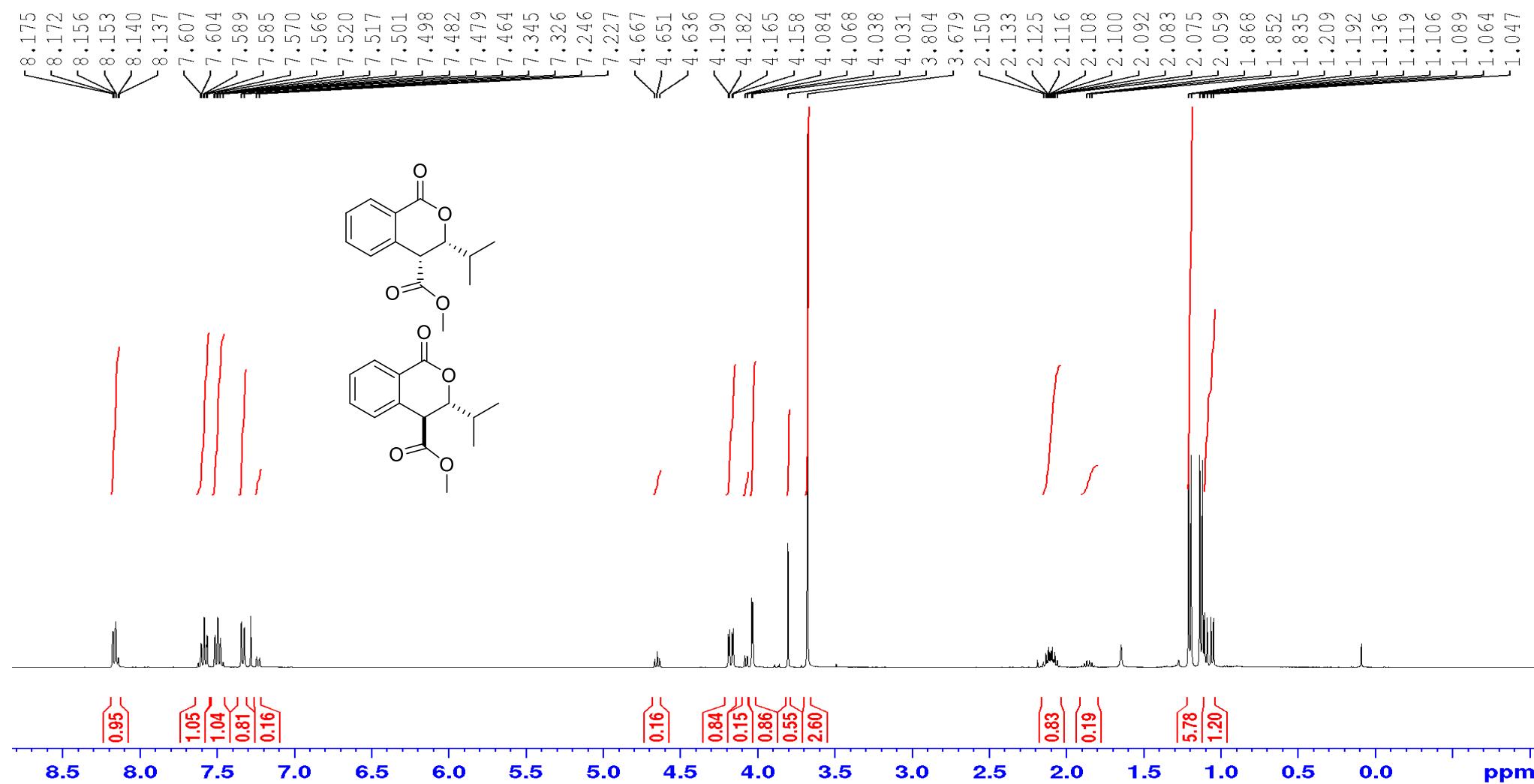
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-33 and *trans*-33



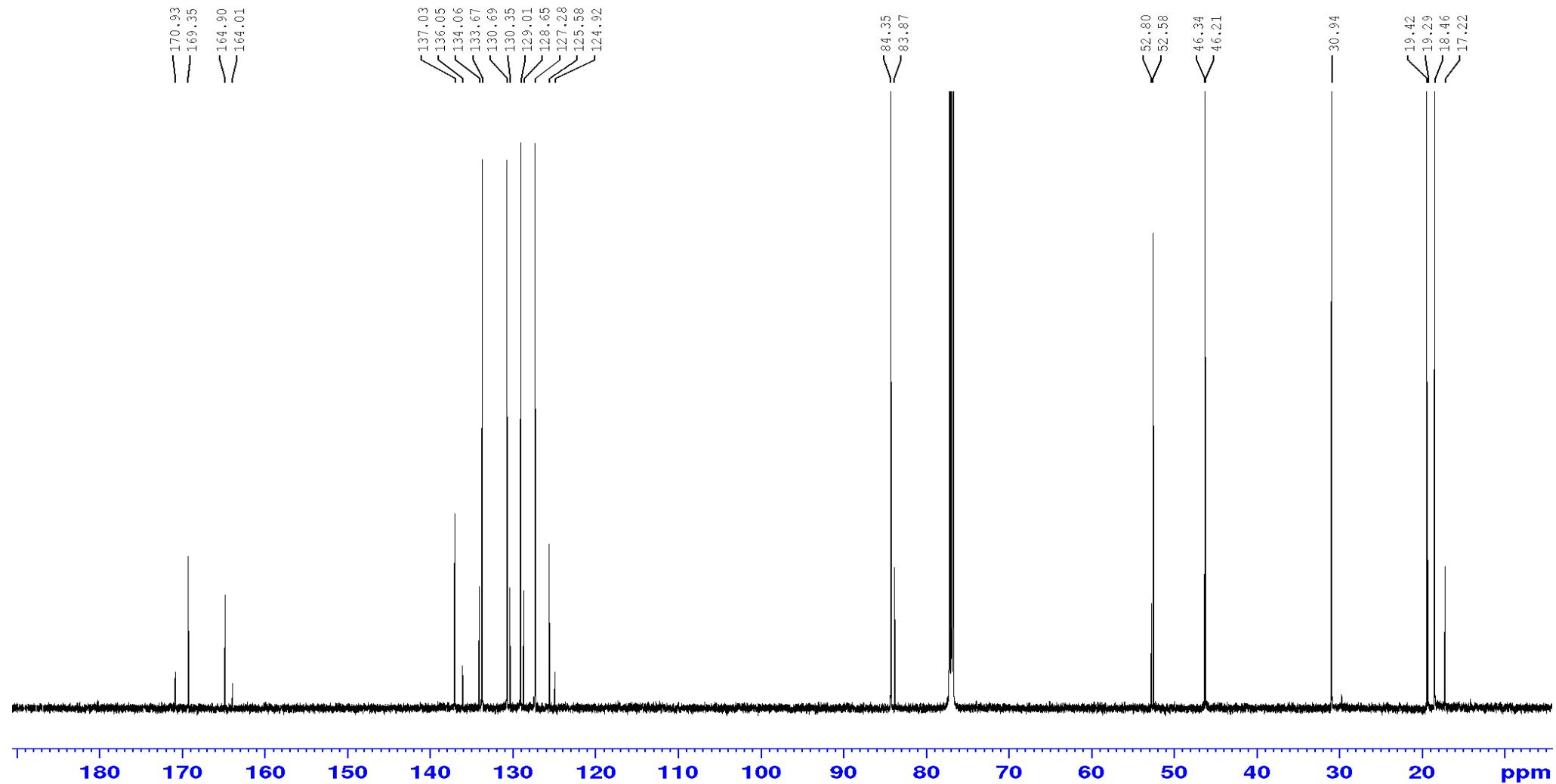
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-33 and *trans*-33



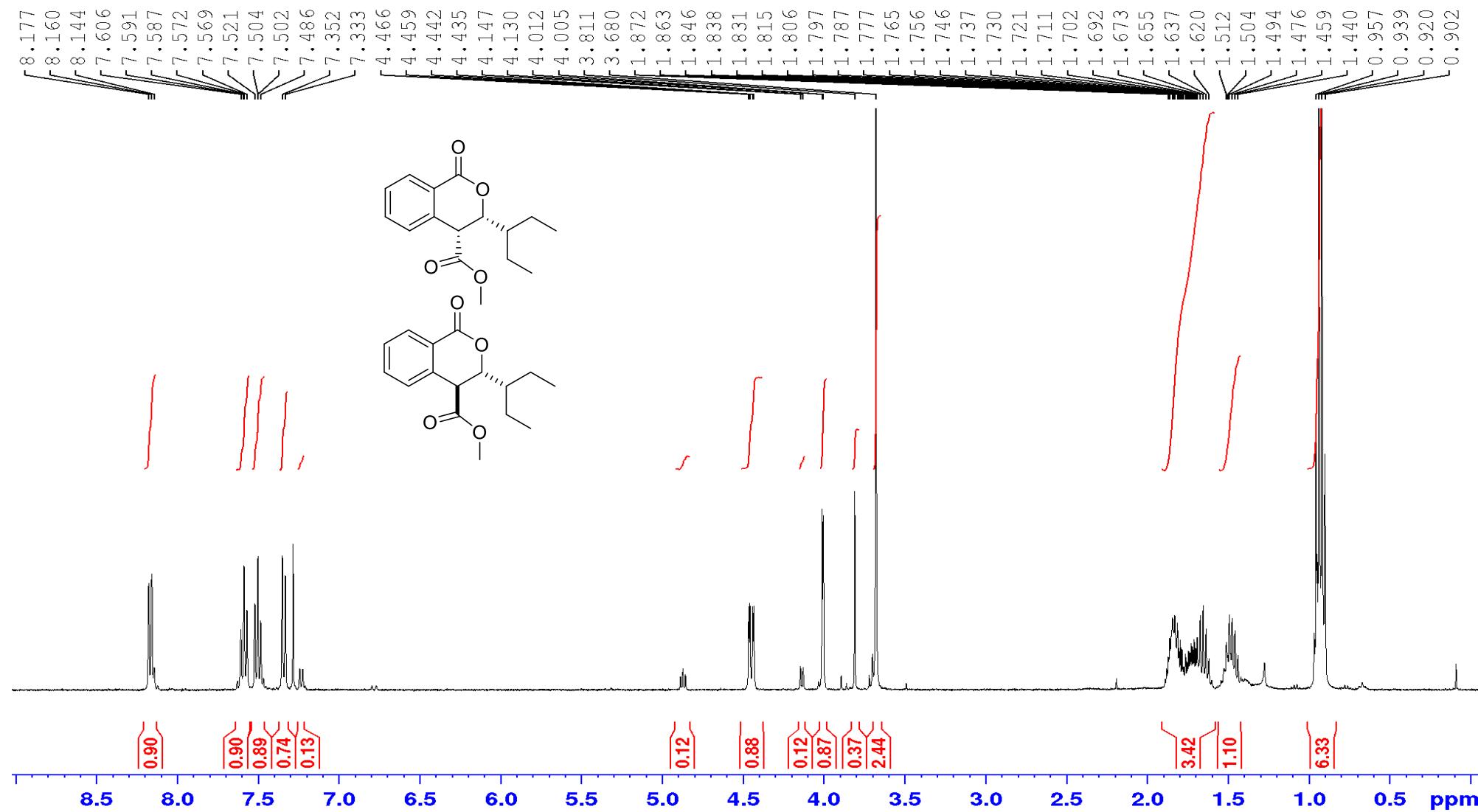
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-34 and *trans*-34



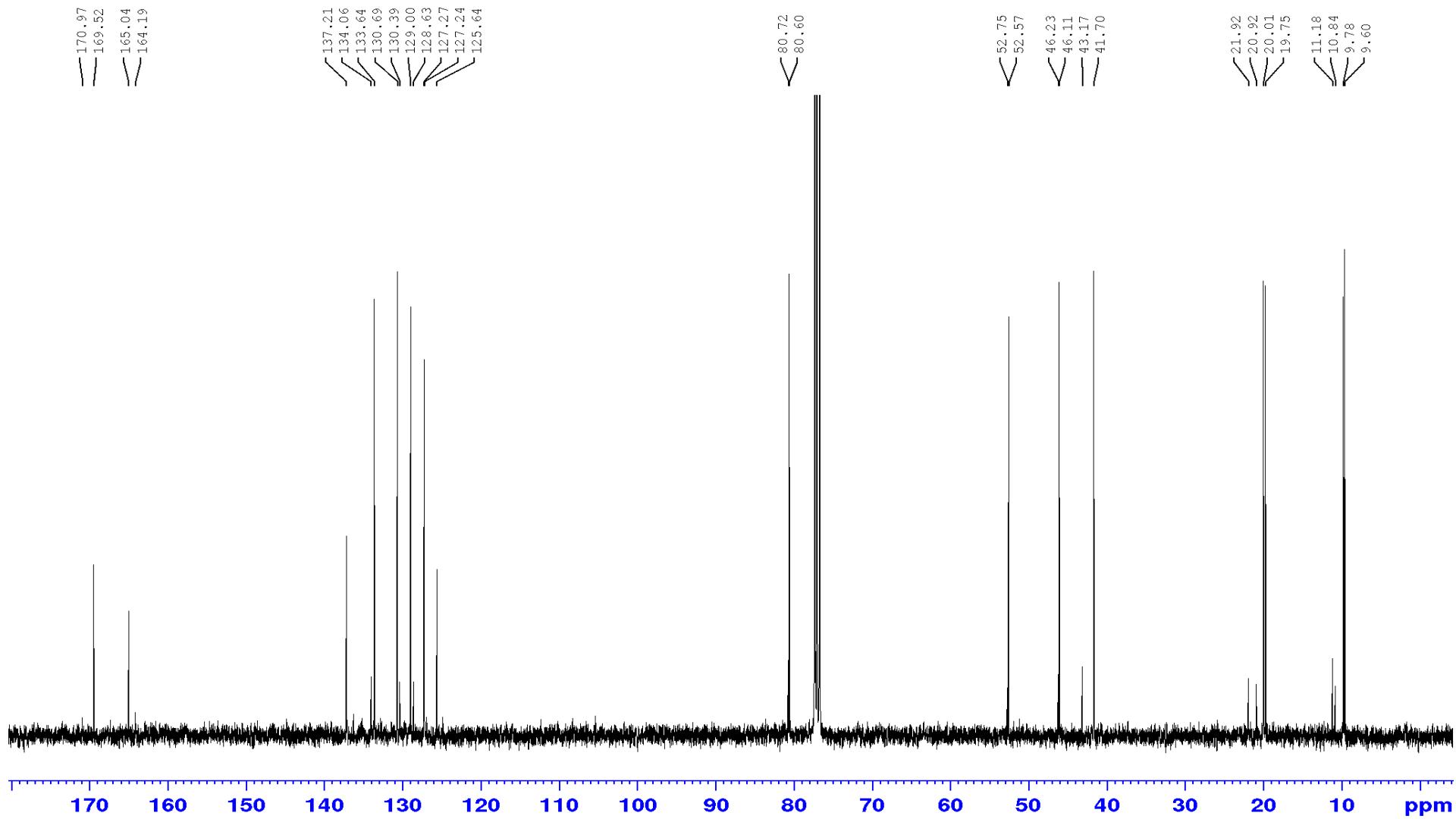
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-34 and *trans*-34



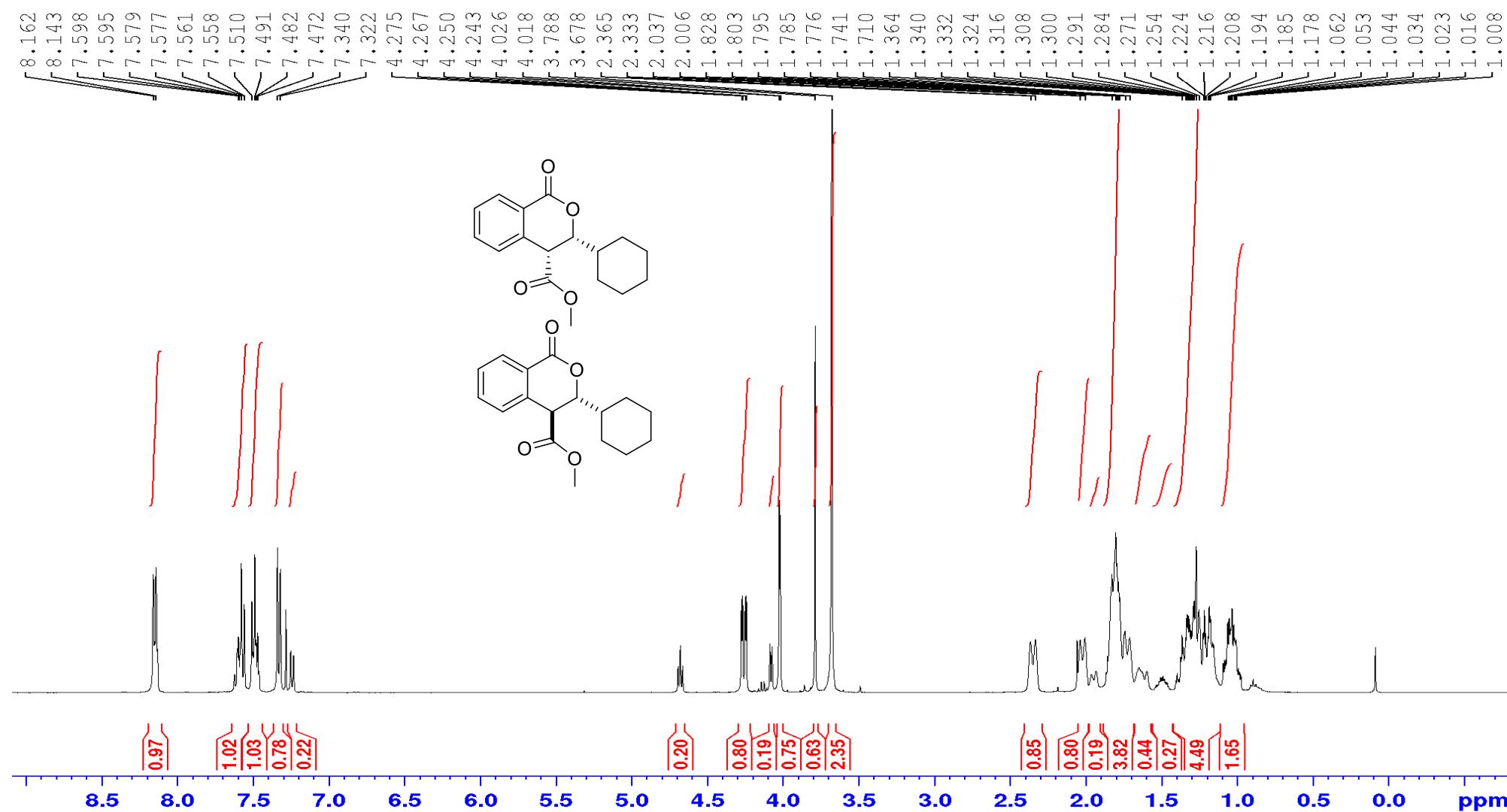
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-35 and *trans*-35



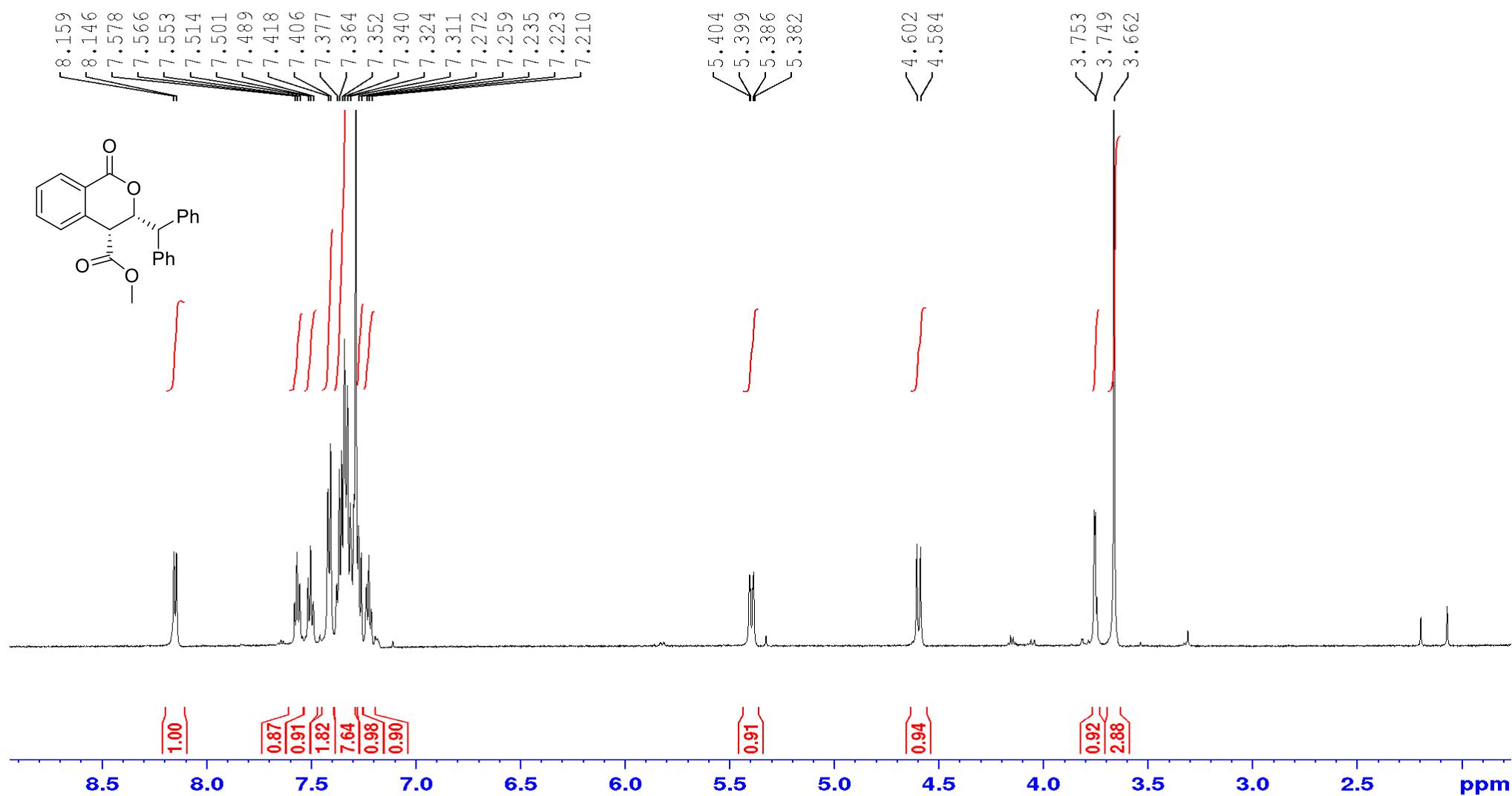
¹³ C NMR (100 MHz, CDCl₃) spectra of *cis*-35 and *trans*-35



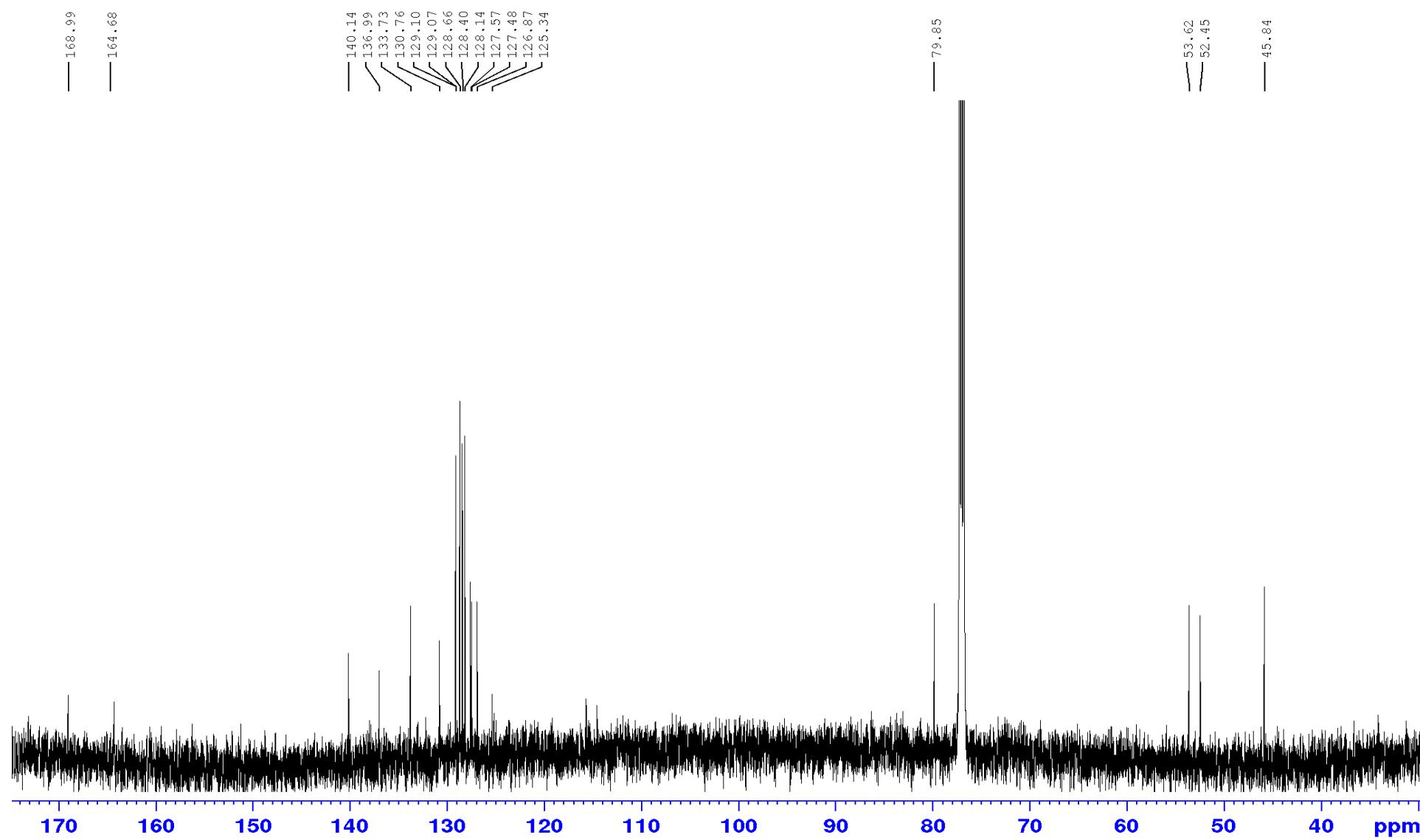
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-36 and *trans*-36



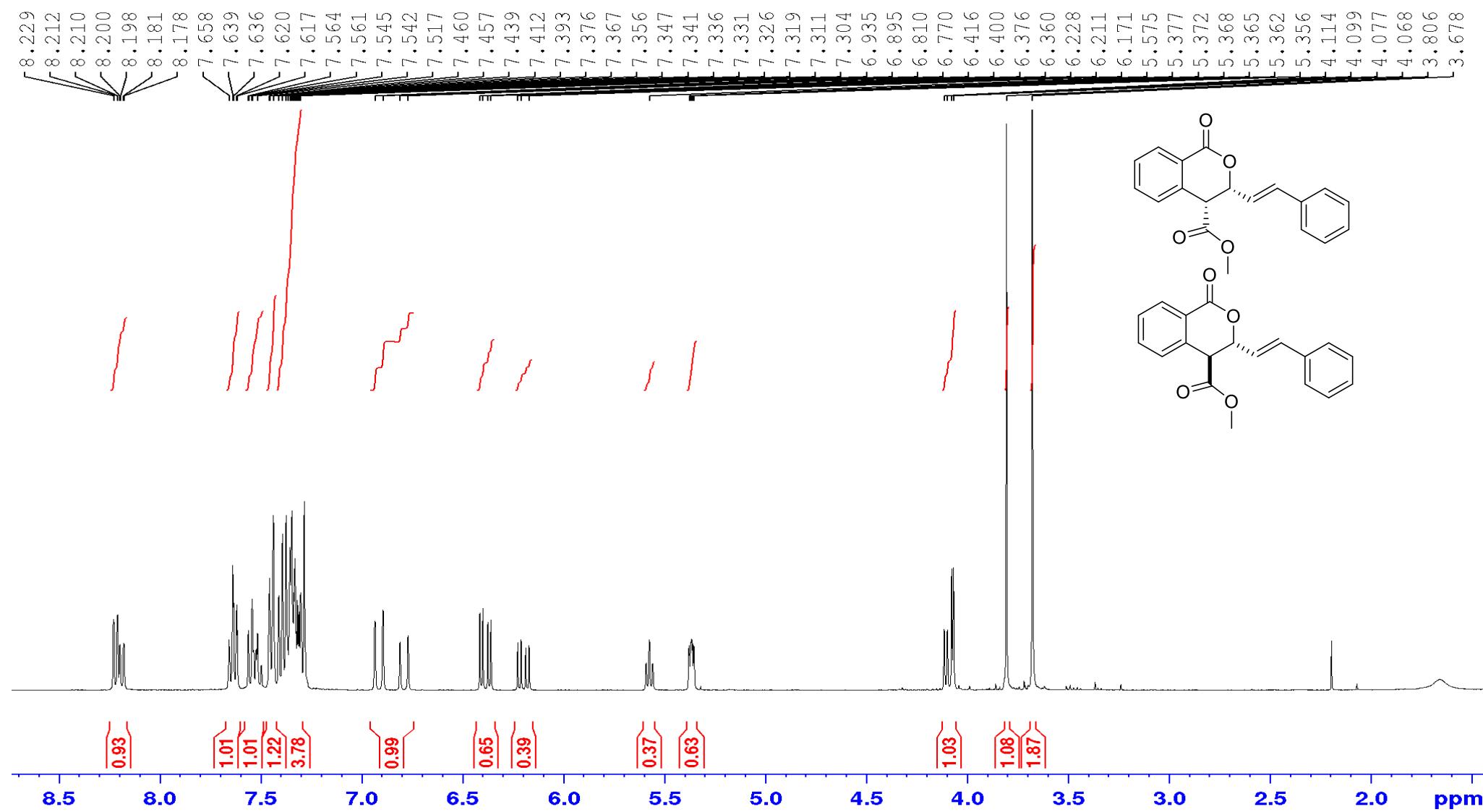
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-37



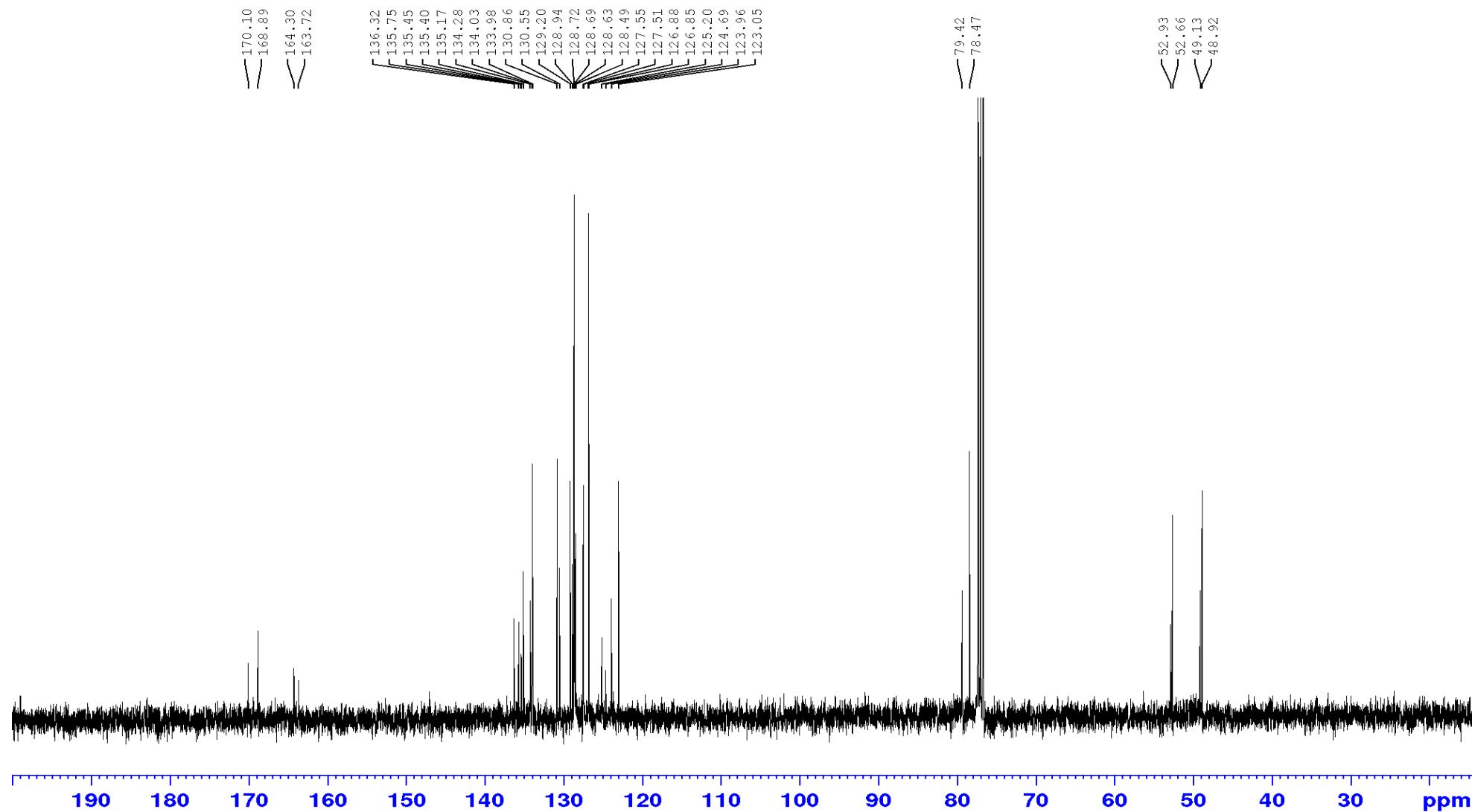
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-37



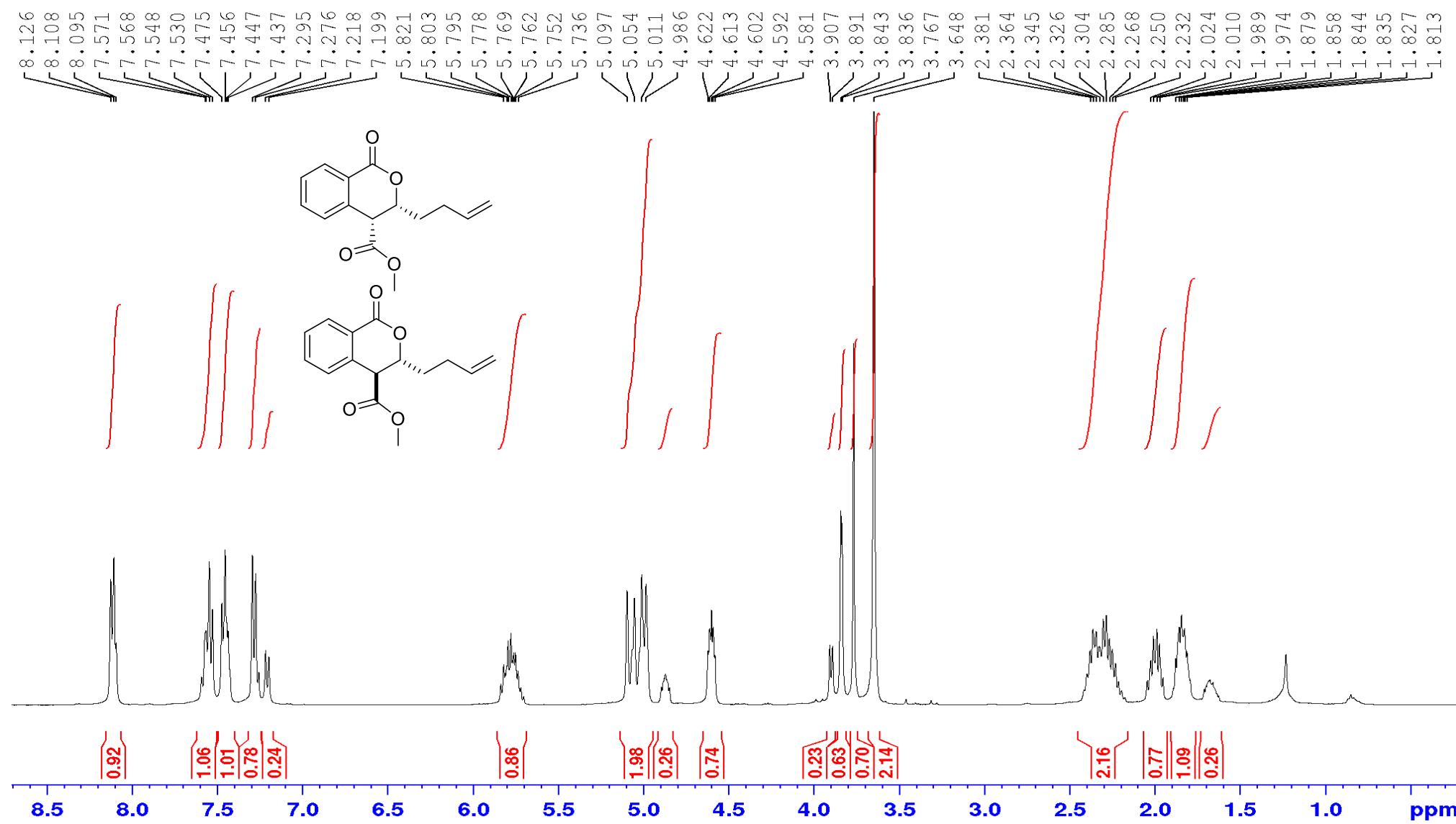
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-38 and *trans*-38



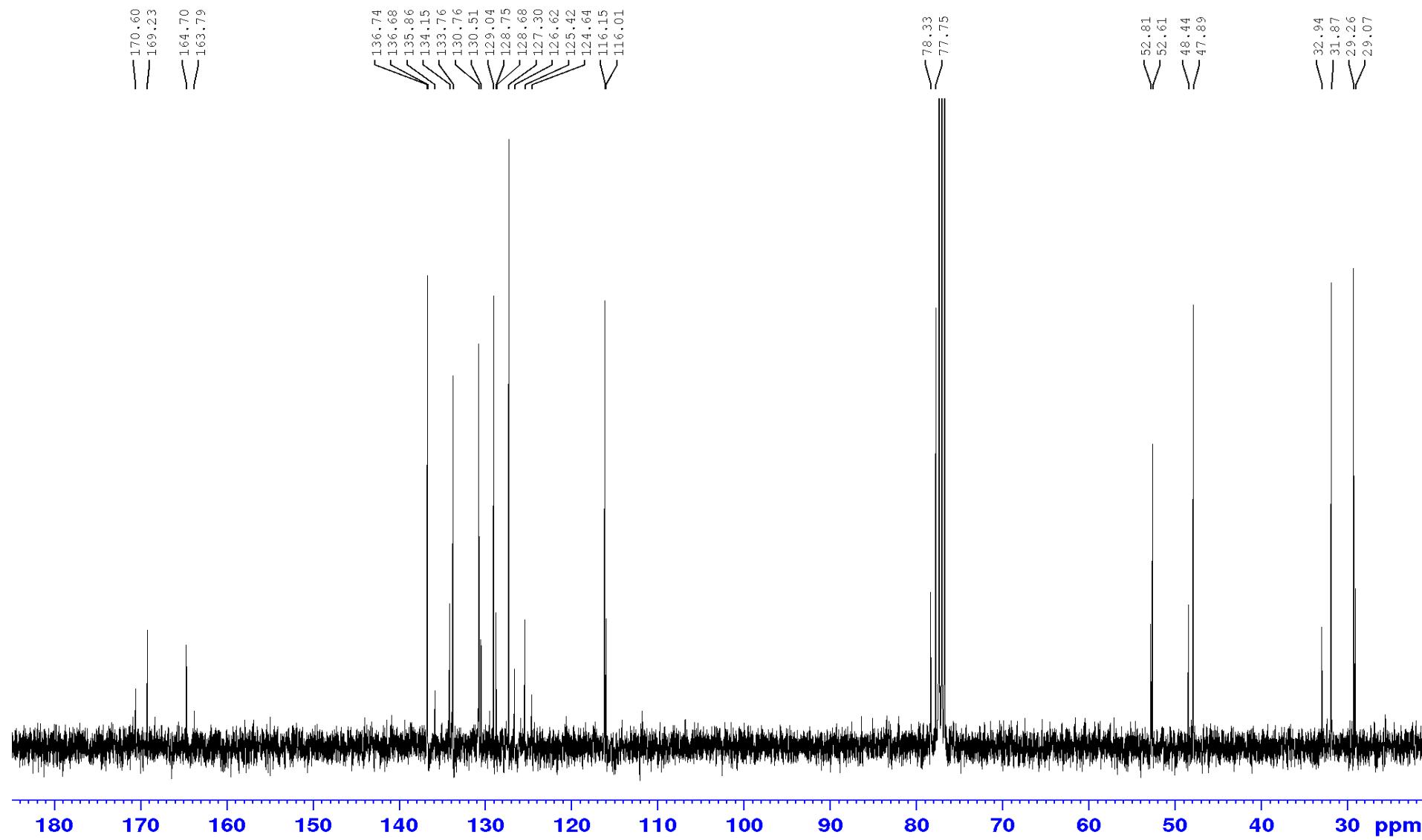
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-38 and *trans*-38



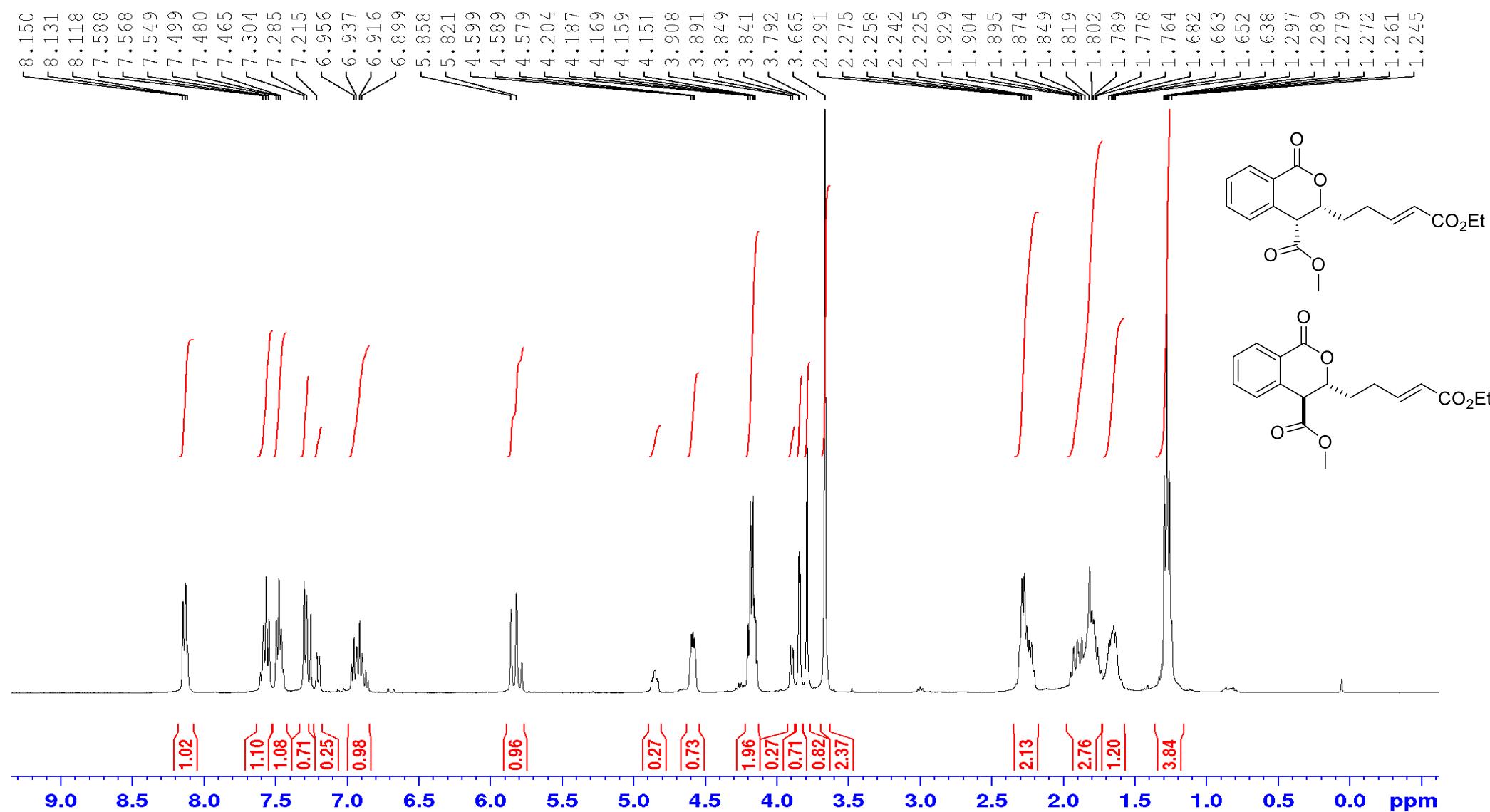
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-39 and *trans*-39



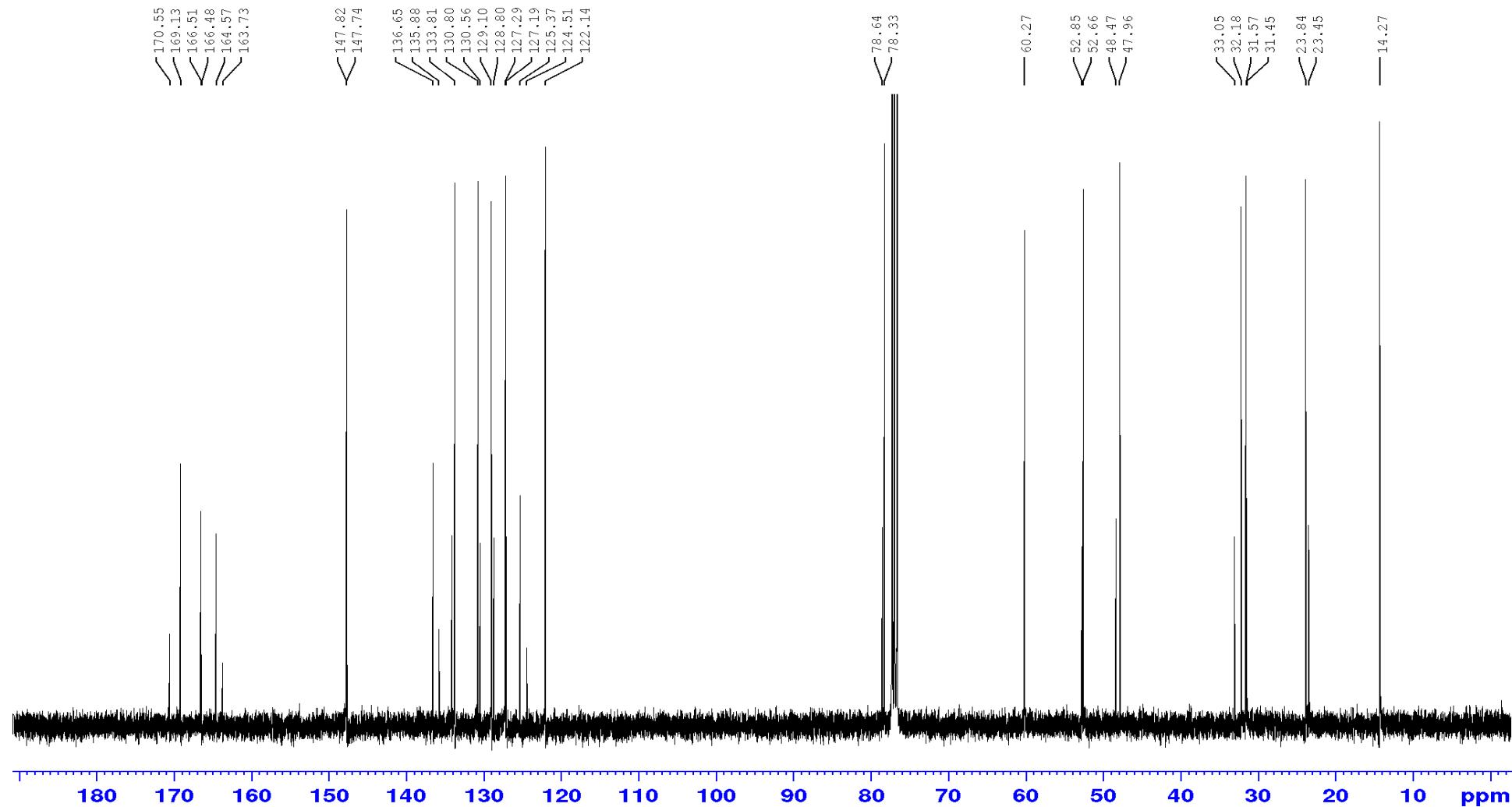
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-39 and *trans*-39



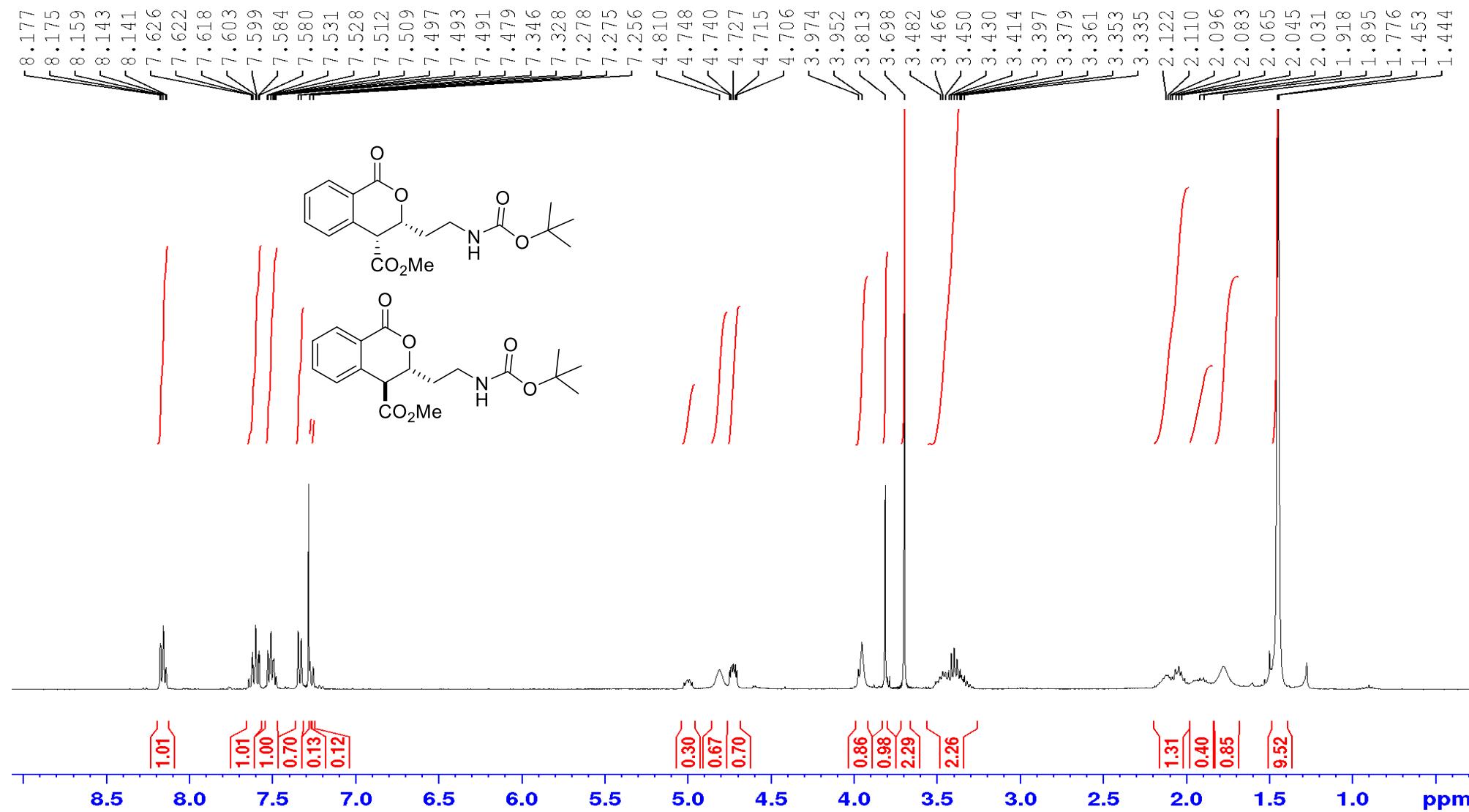
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-40 and *trans*-40



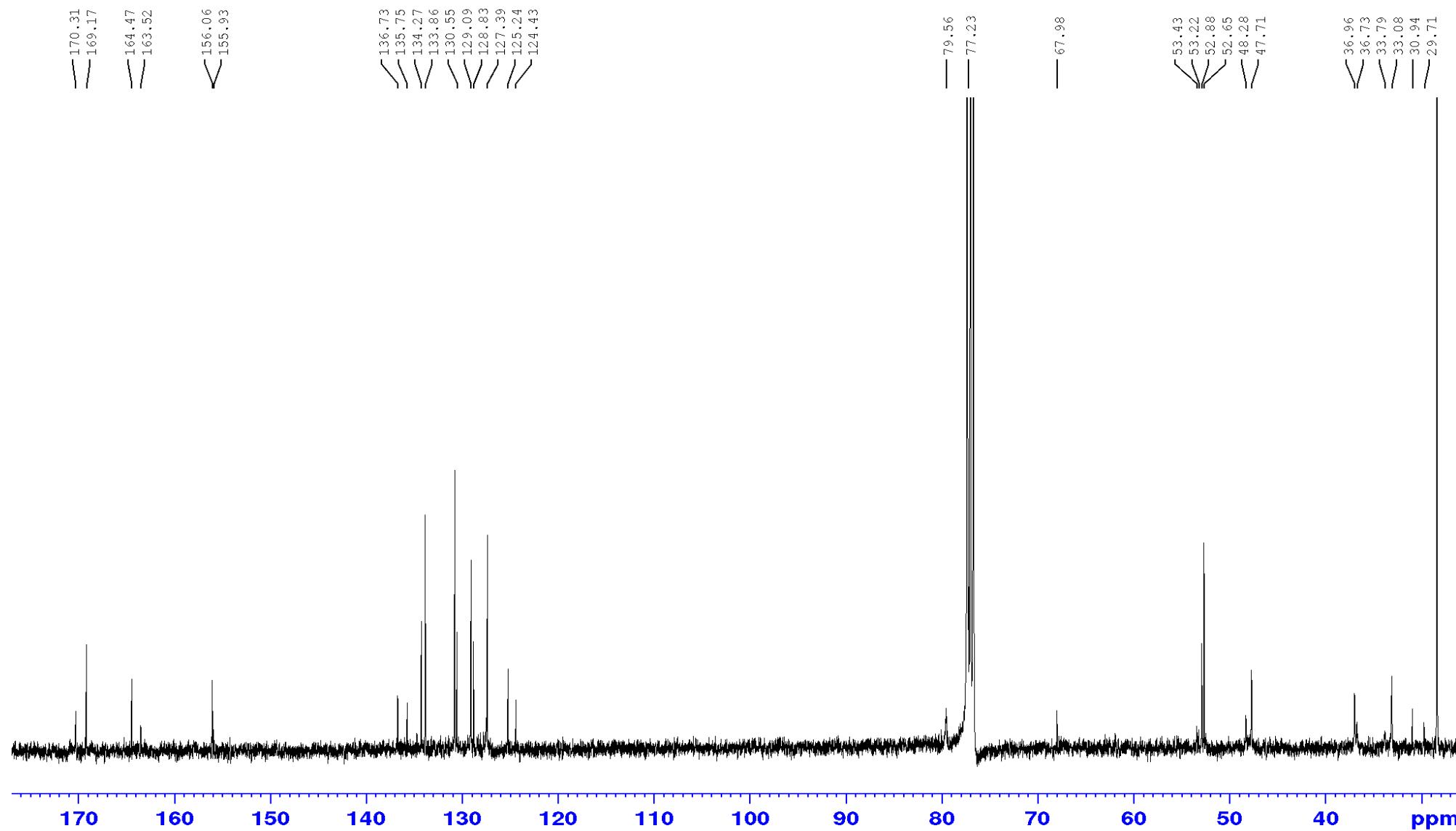
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-40



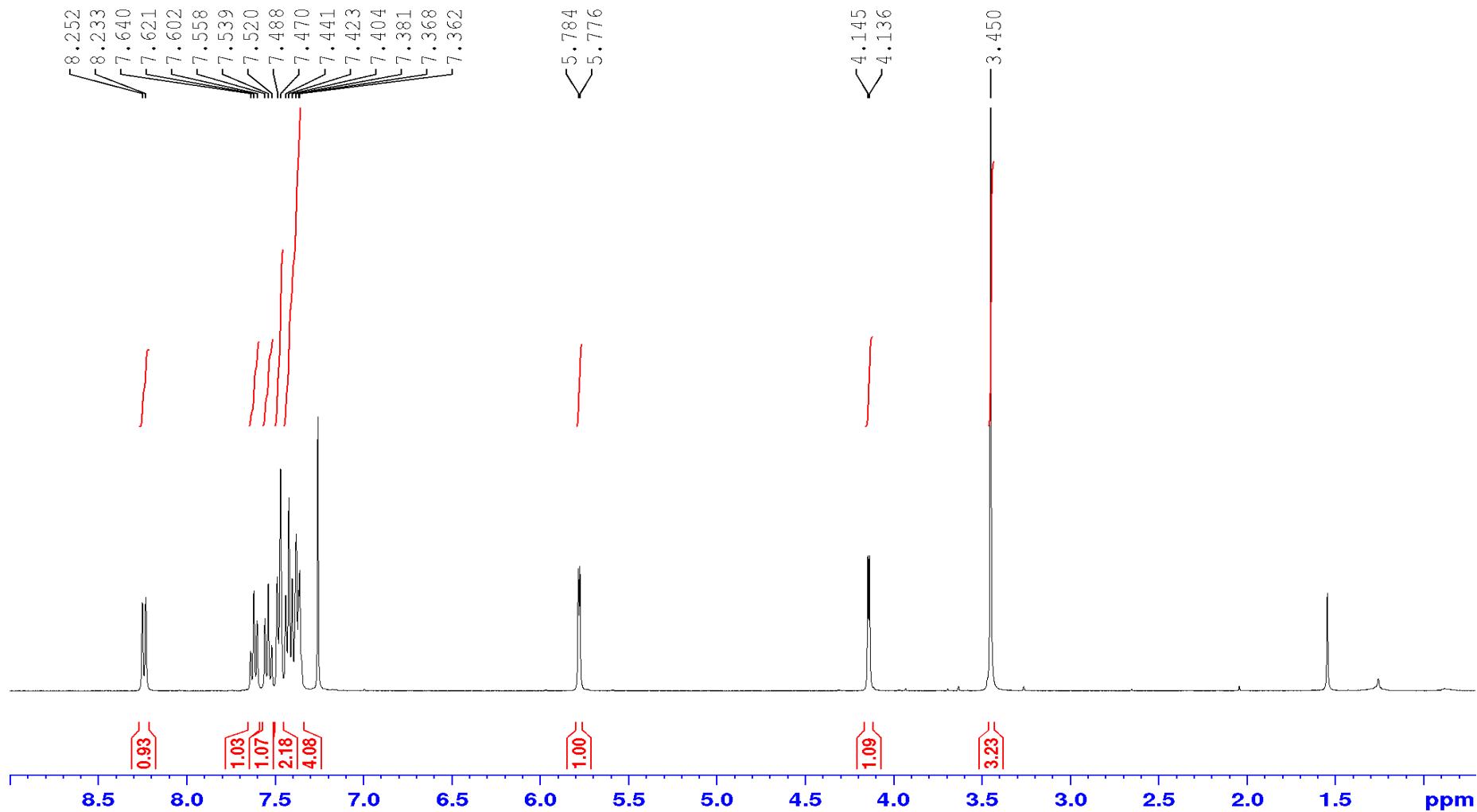
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-41



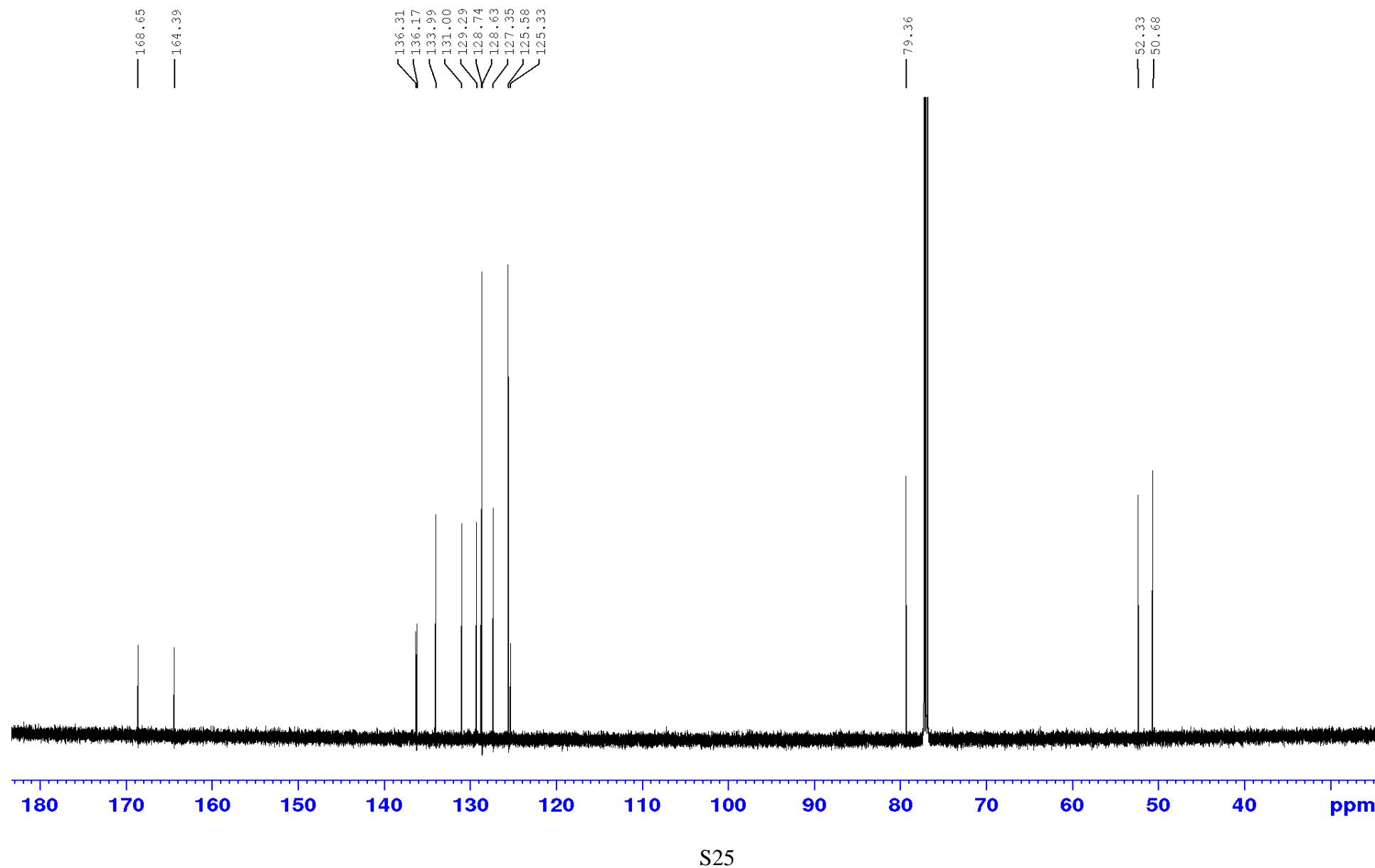
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-41



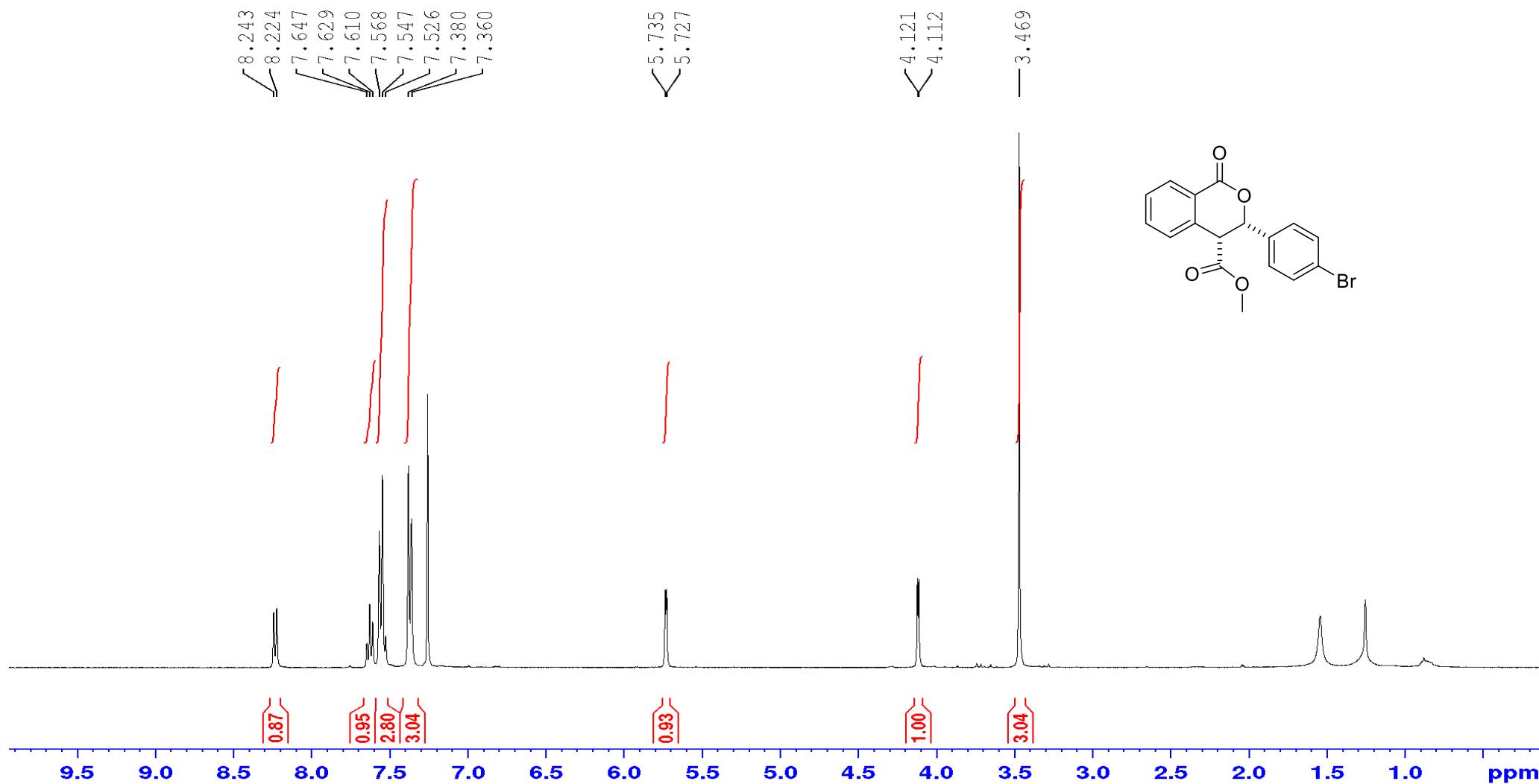
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-42



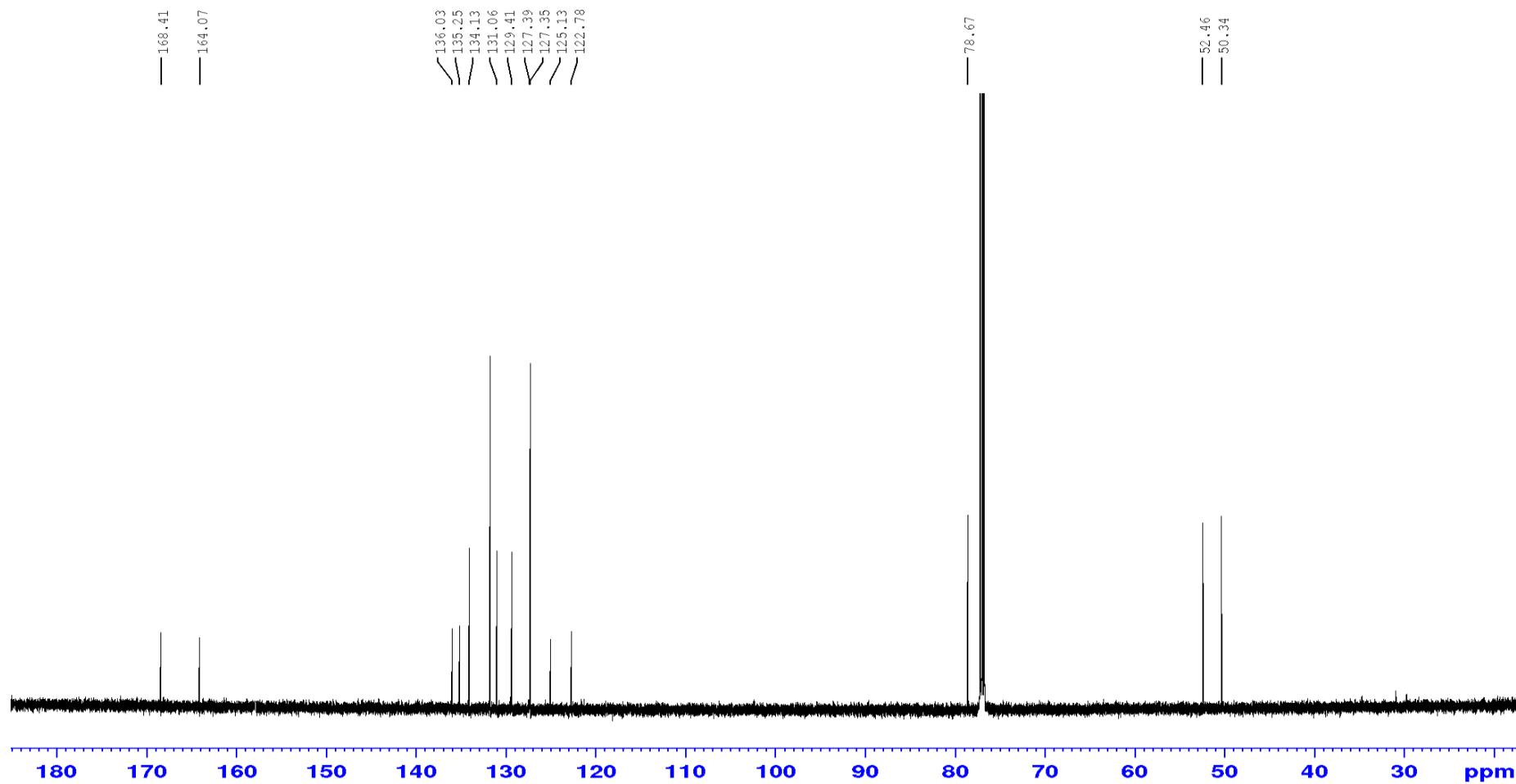
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-42



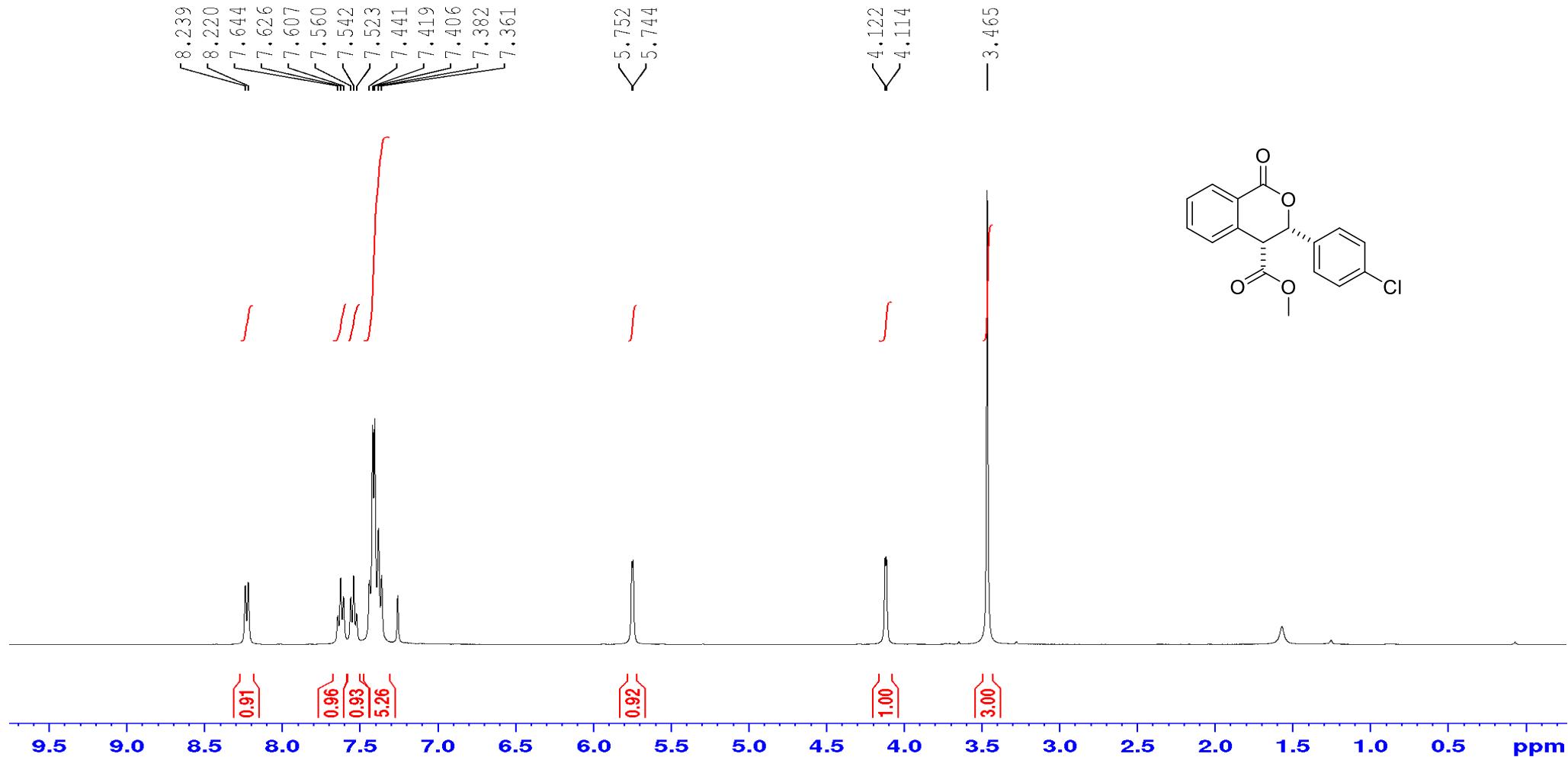
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-43



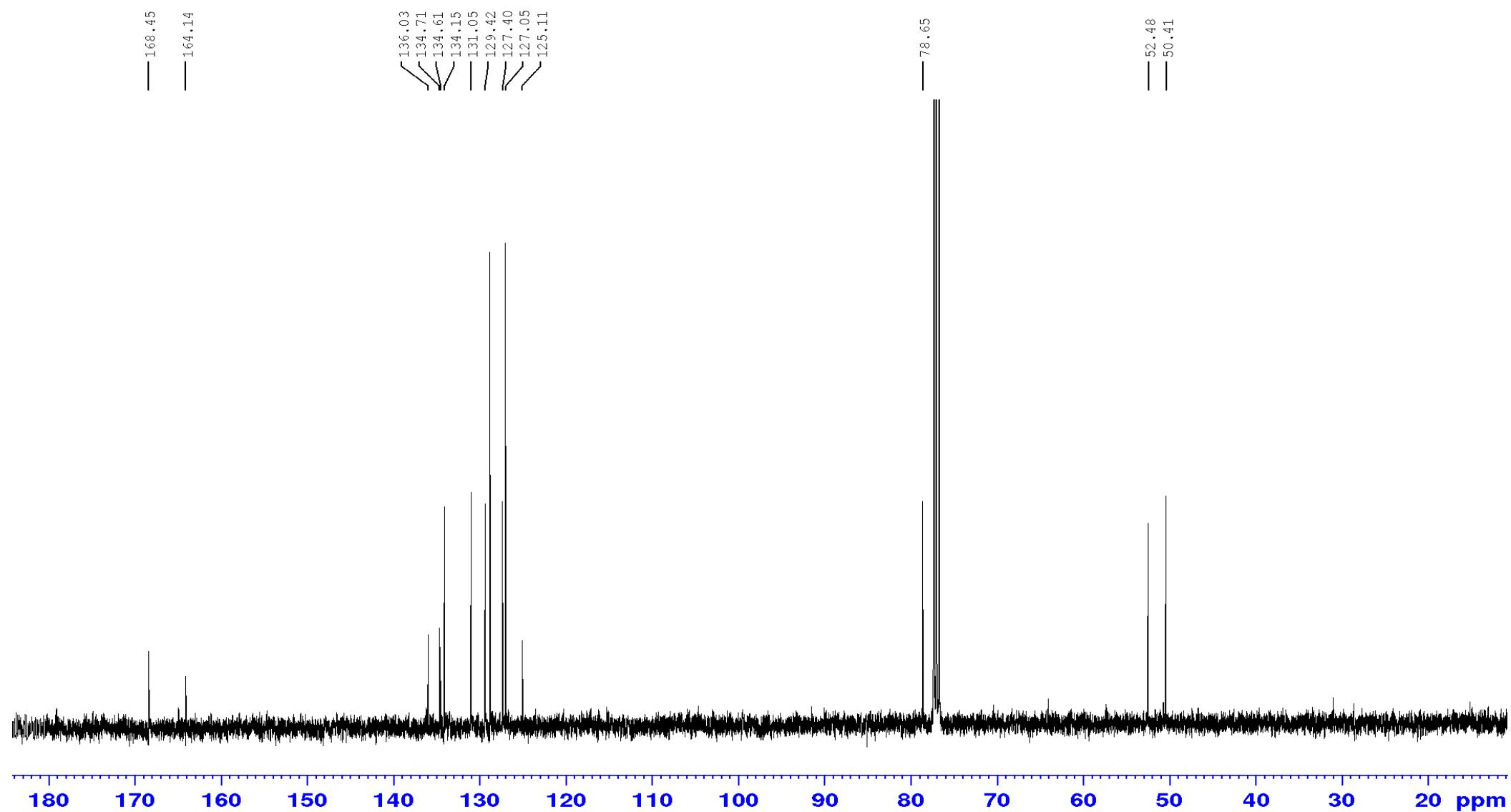
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-43



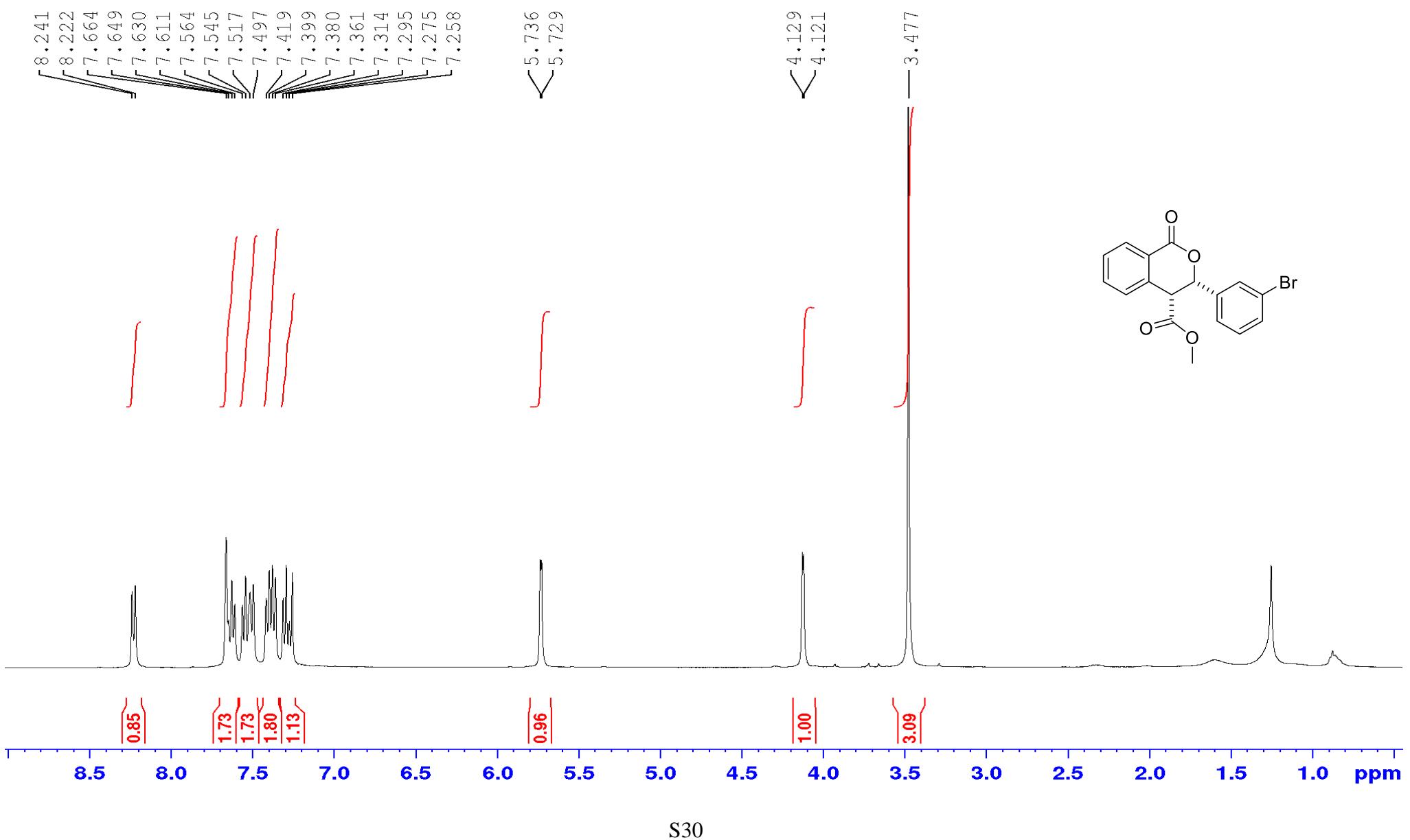
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-44



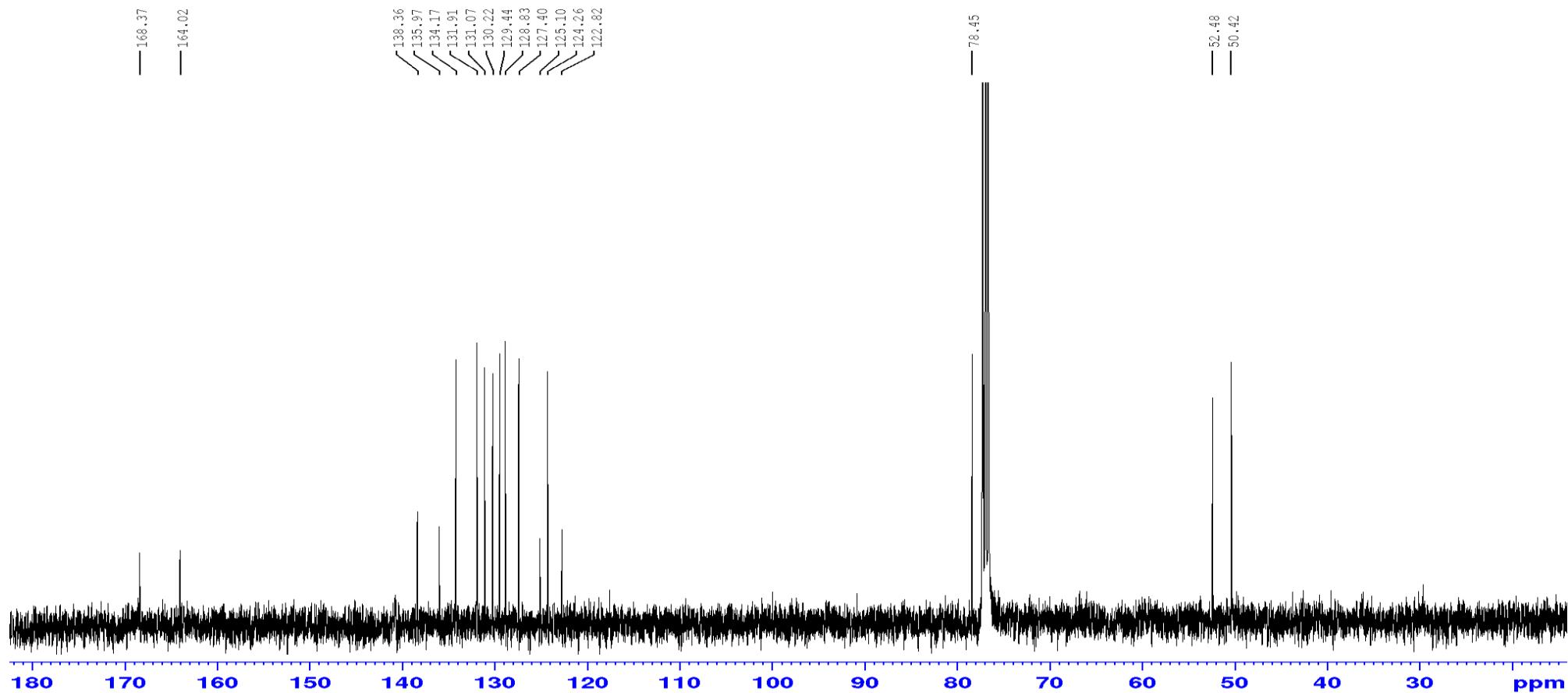
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-44



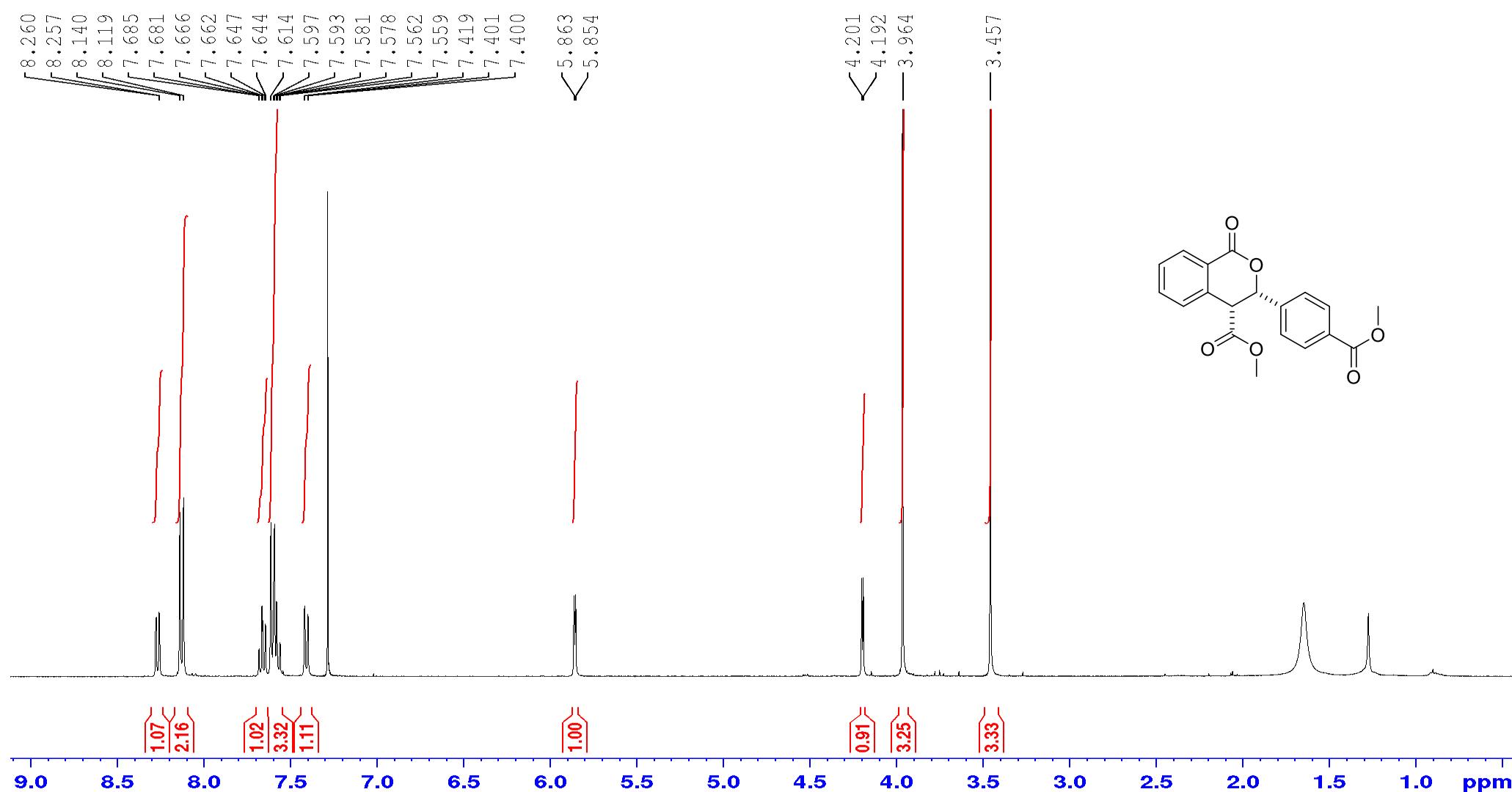
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-45



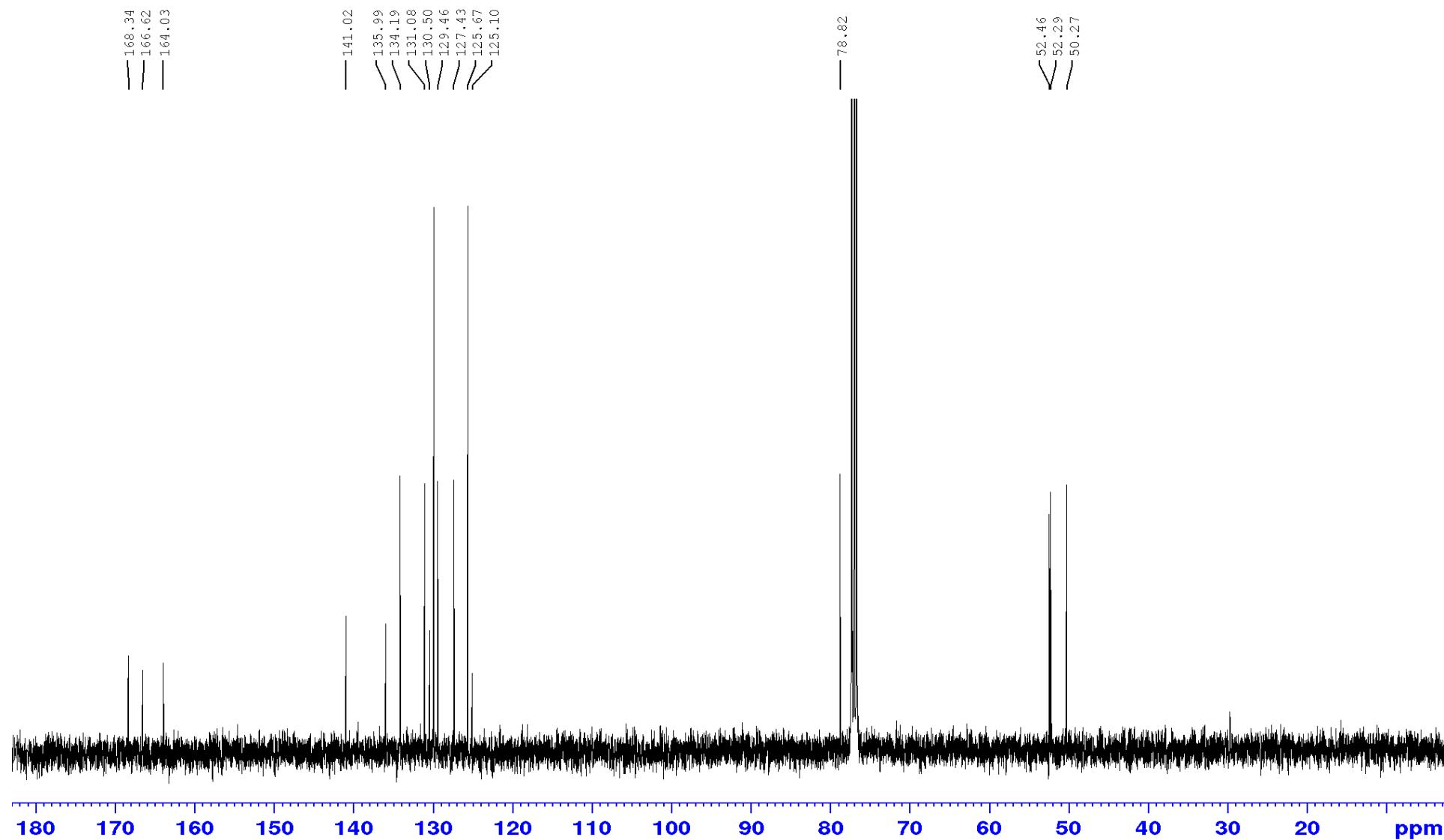
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-45



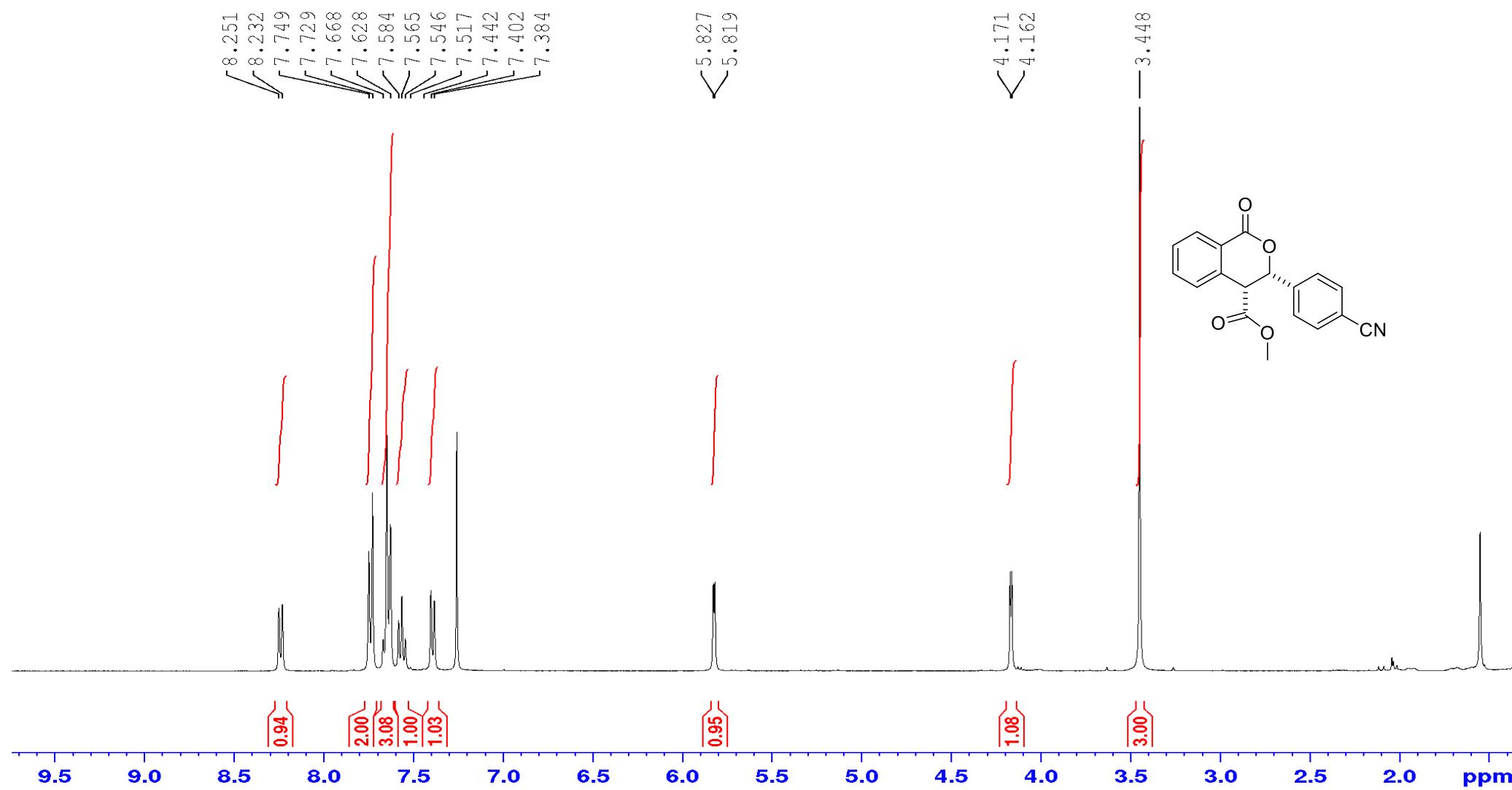
¹H NMR (400 MHz, CDCl₃) spectra of cis-46



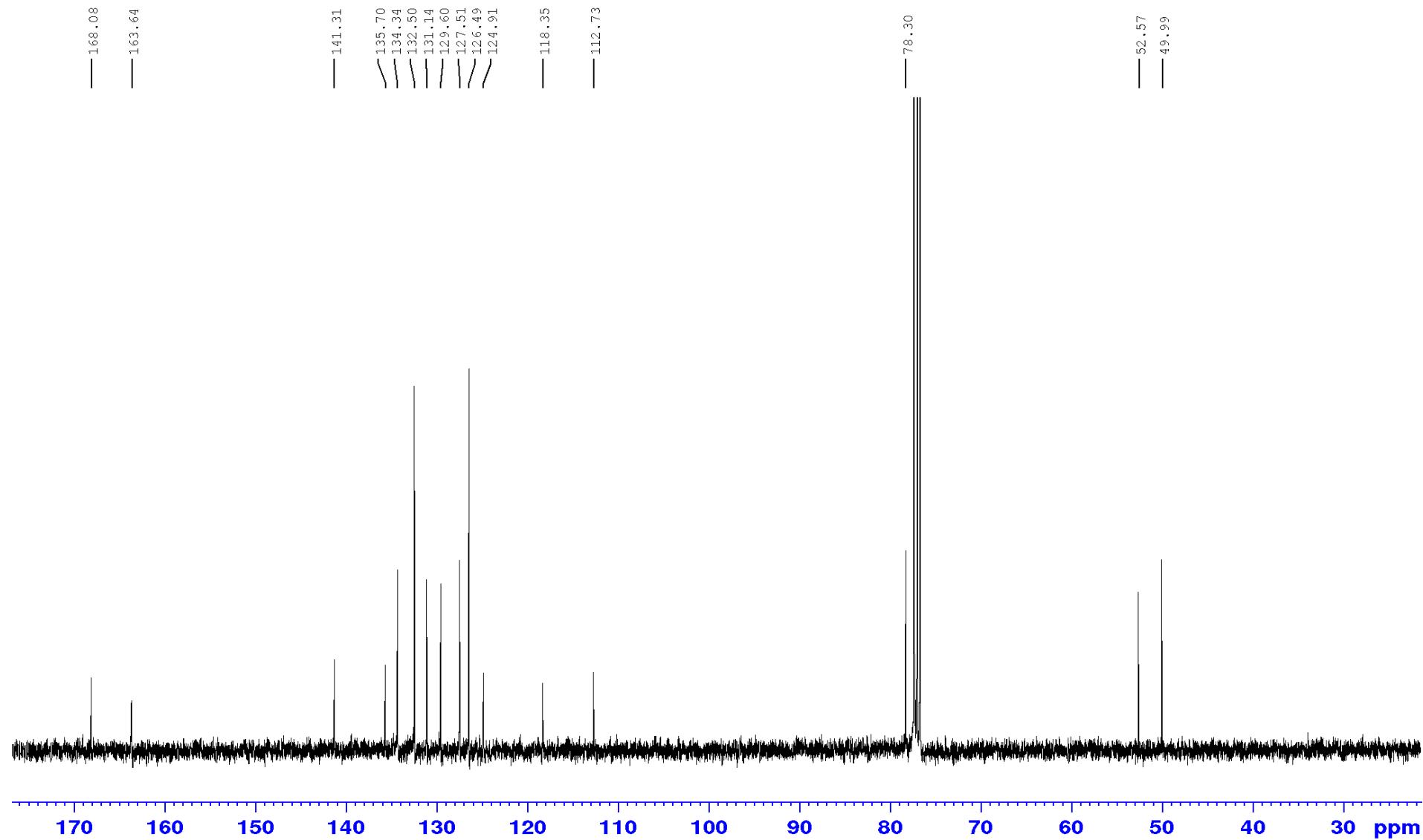
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-46



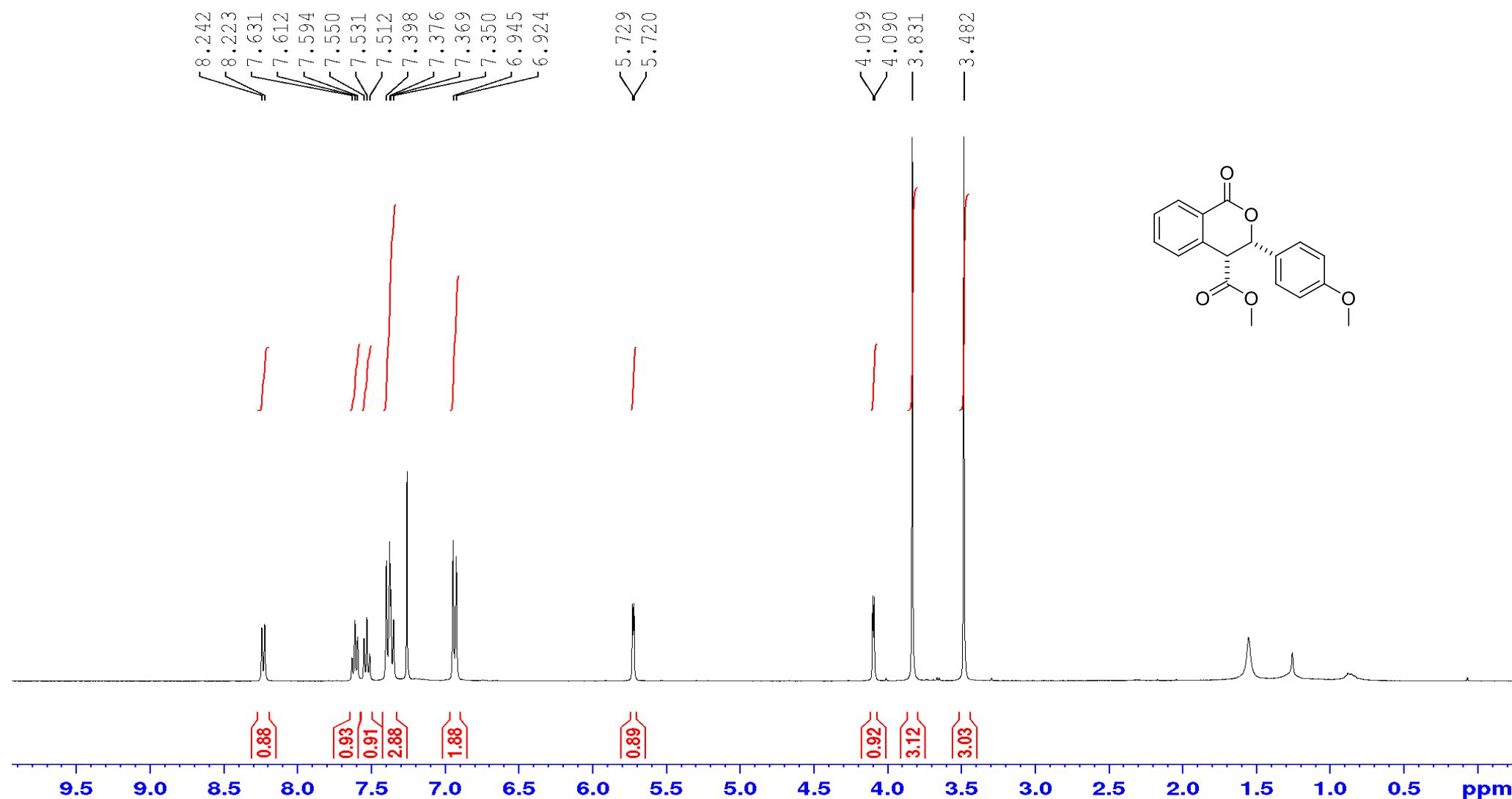
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-47



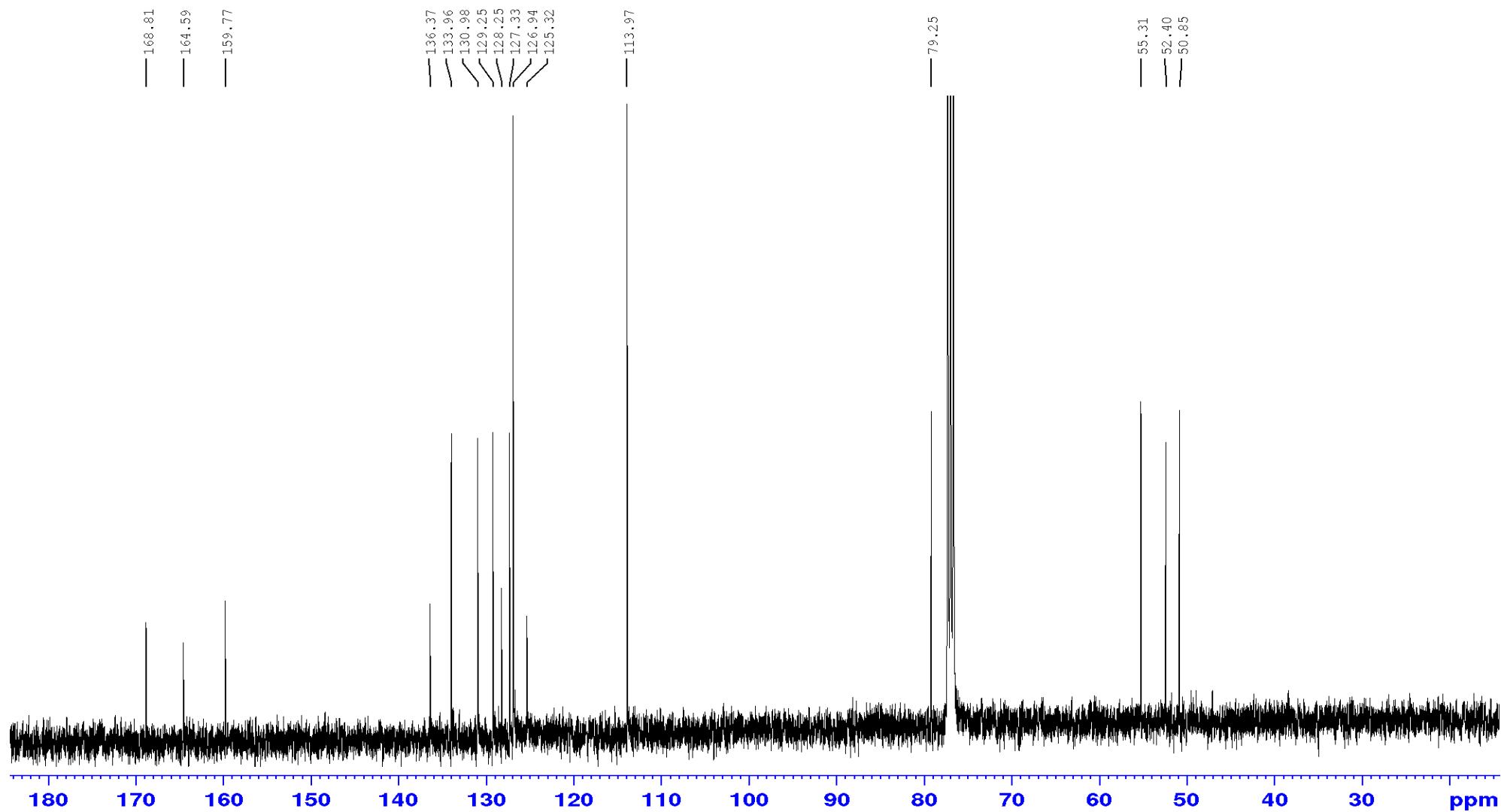
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-47



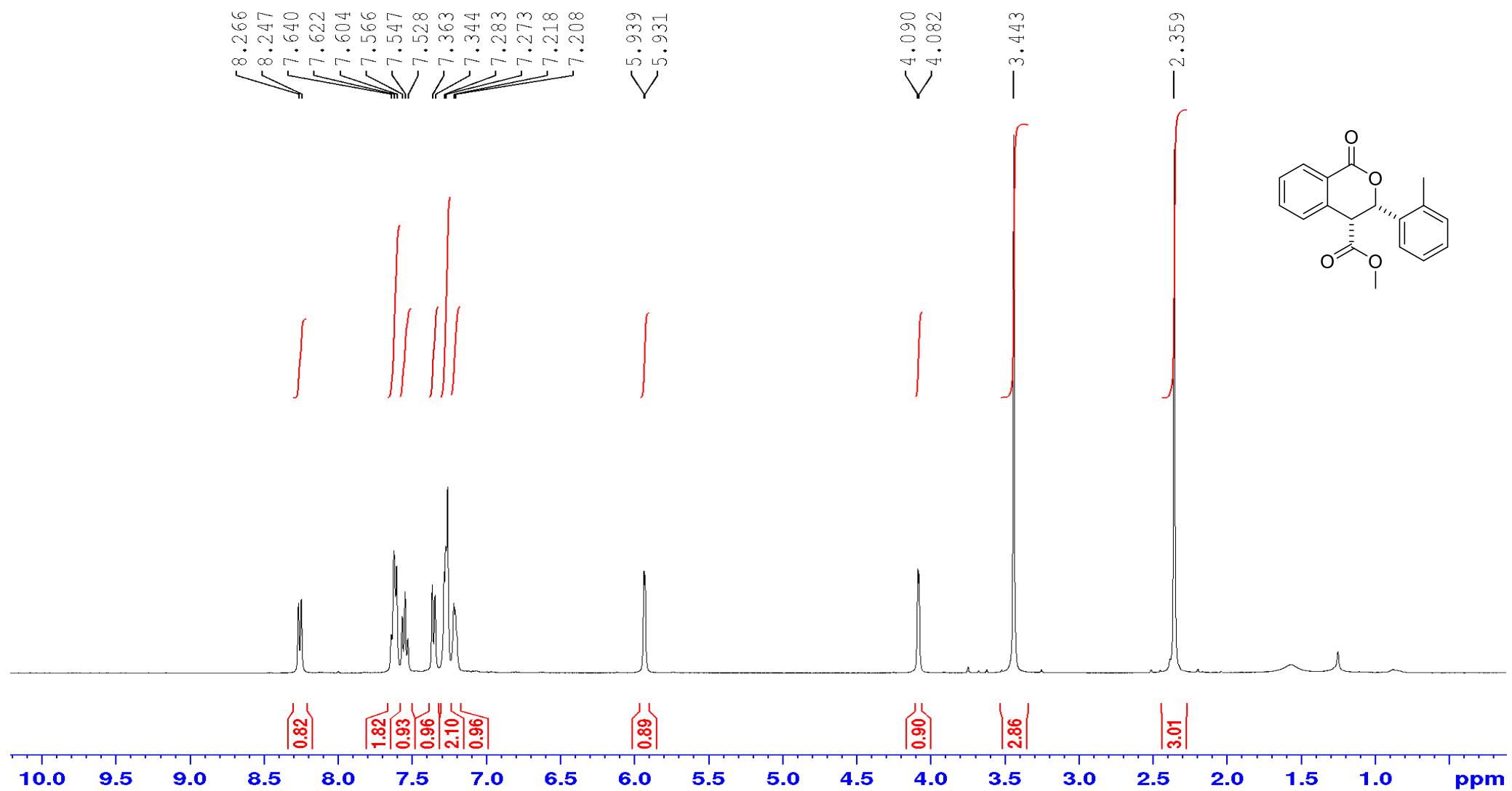
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-48



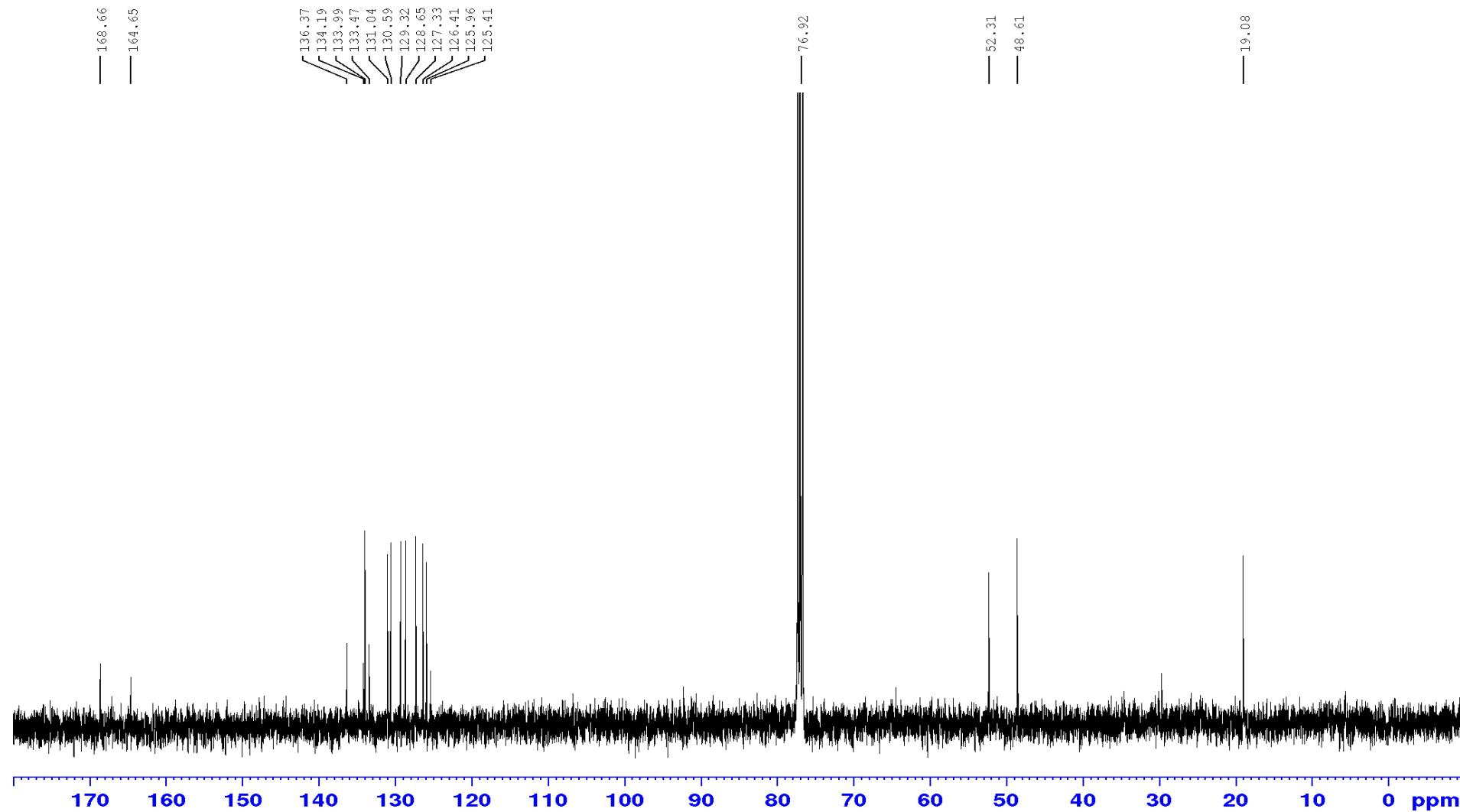
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-48



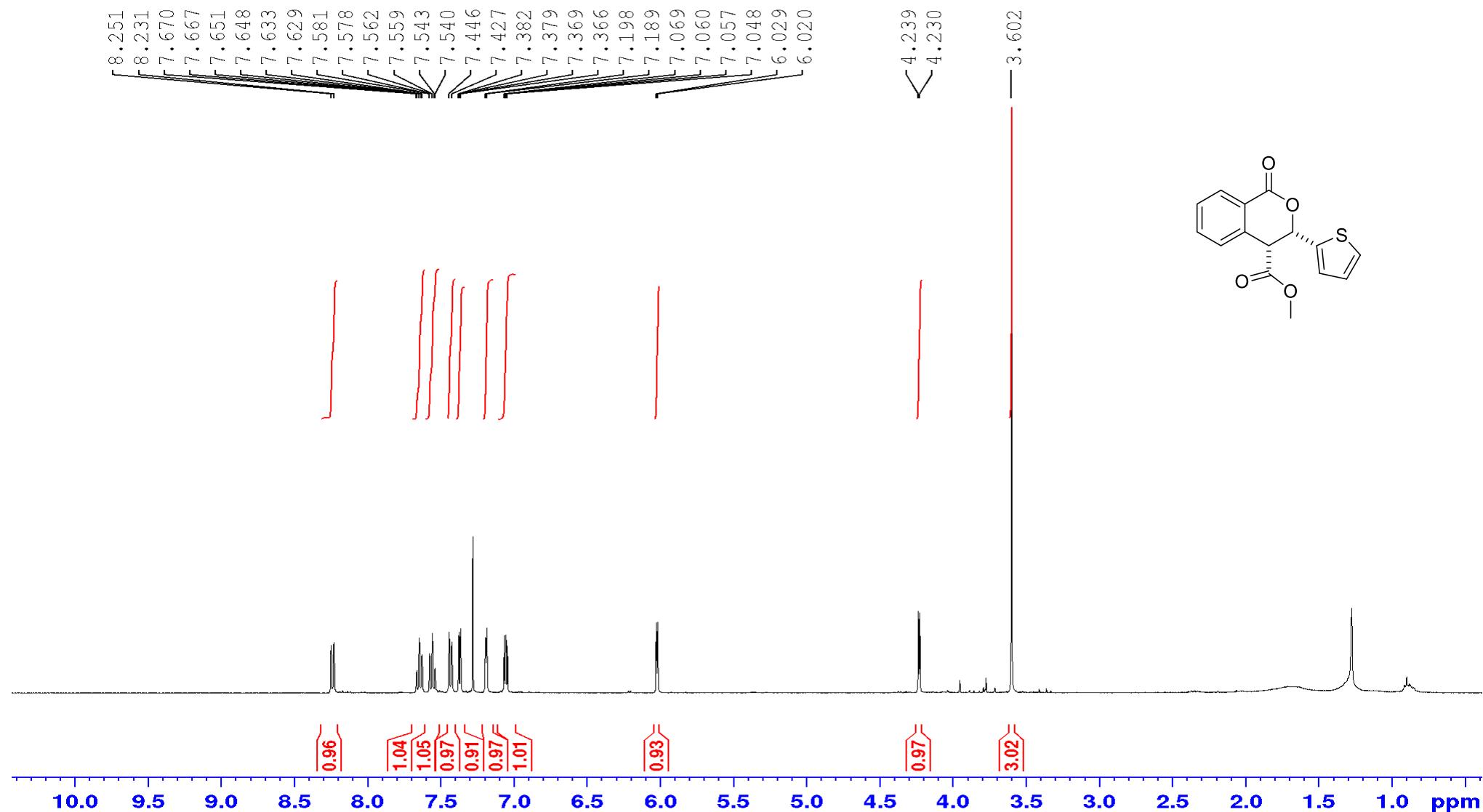
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-49



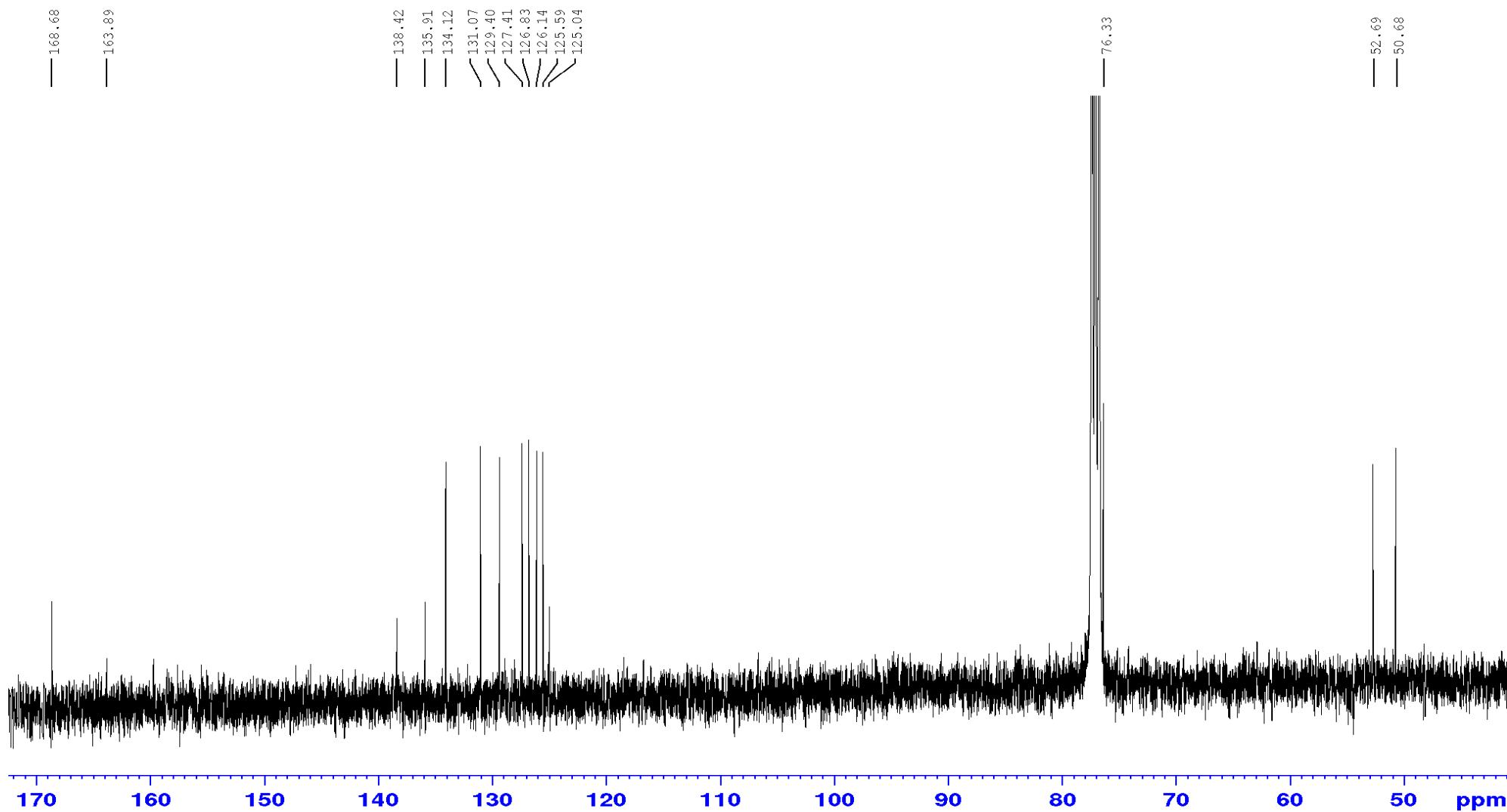
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-49



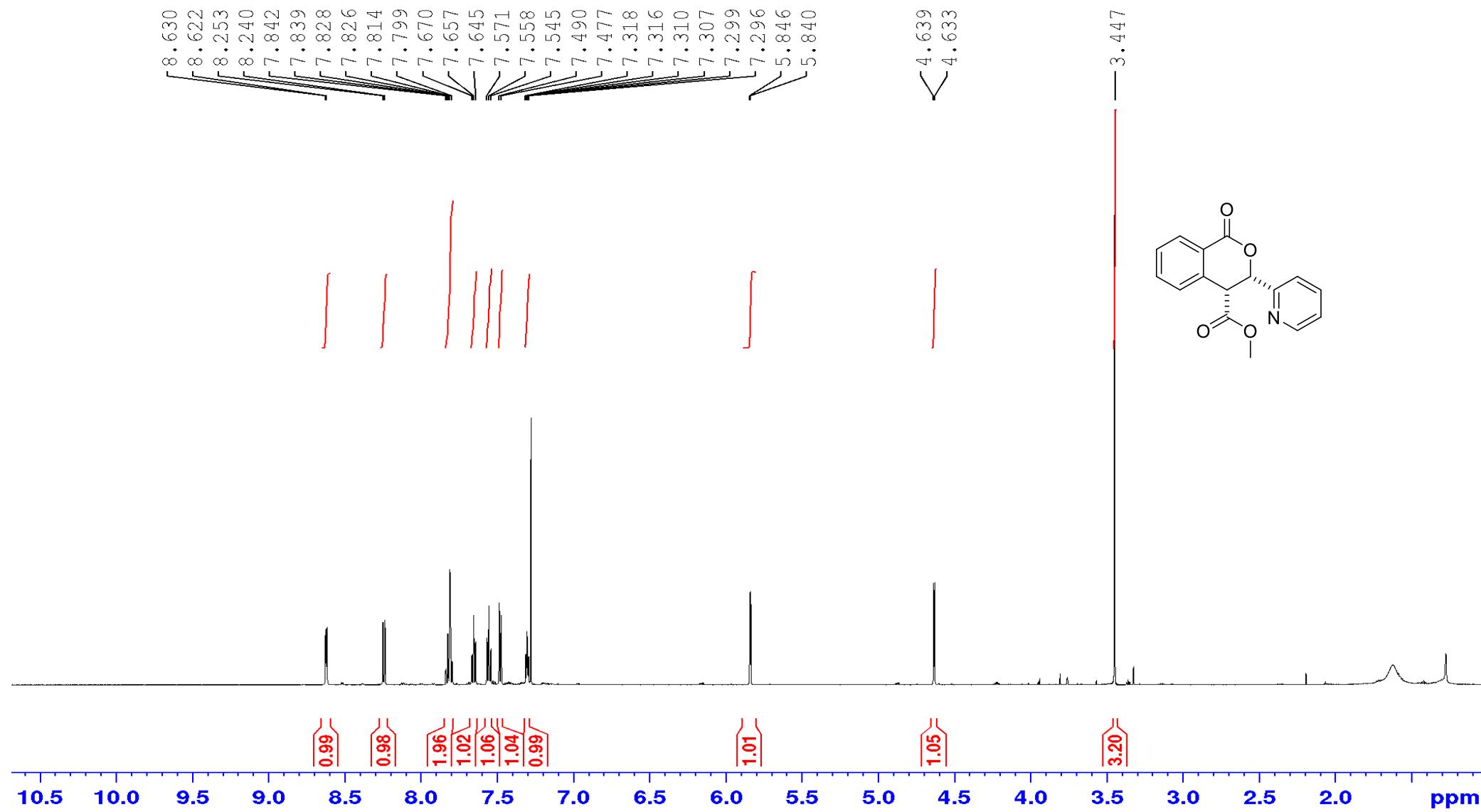
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-50



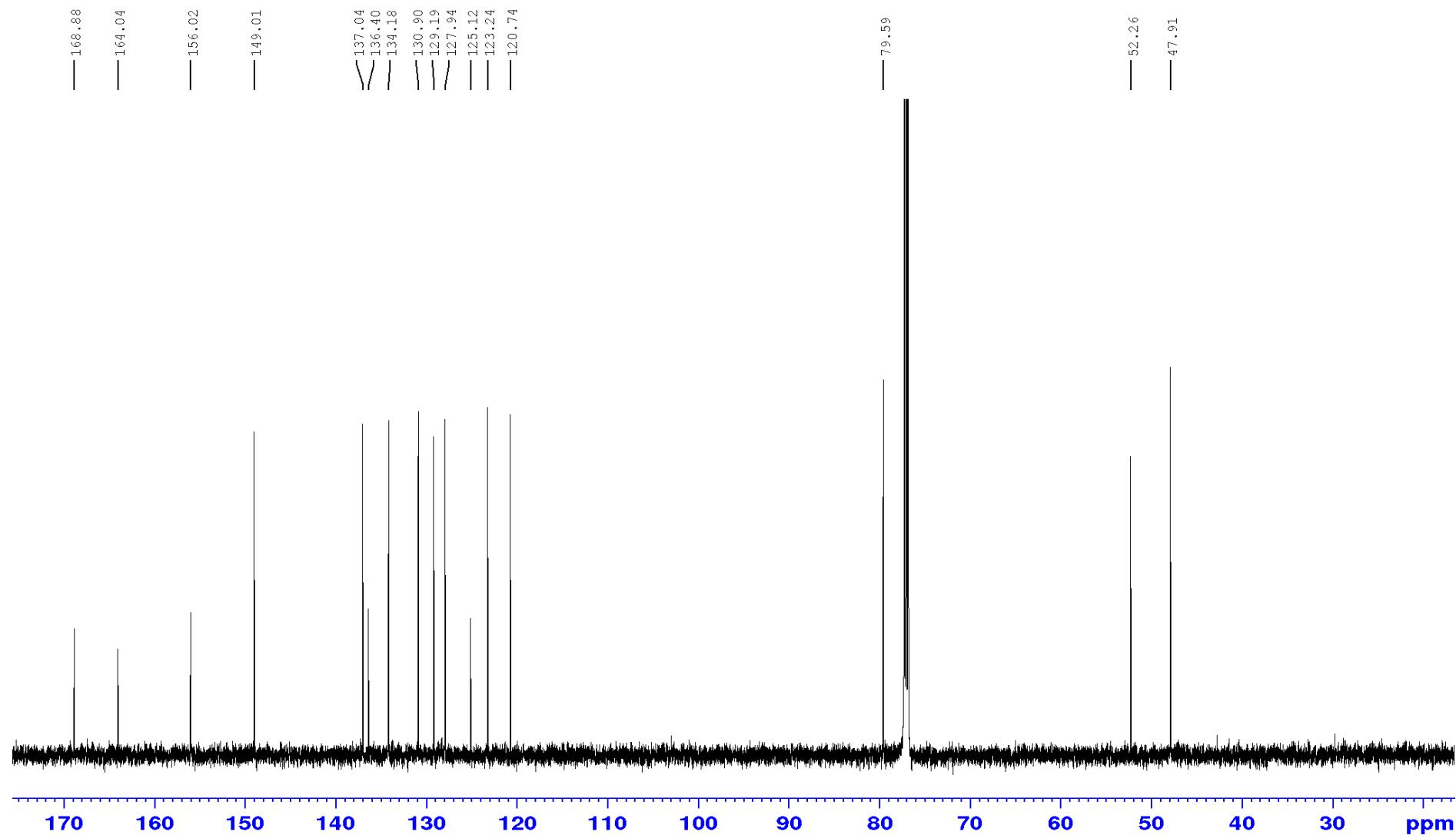
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-50



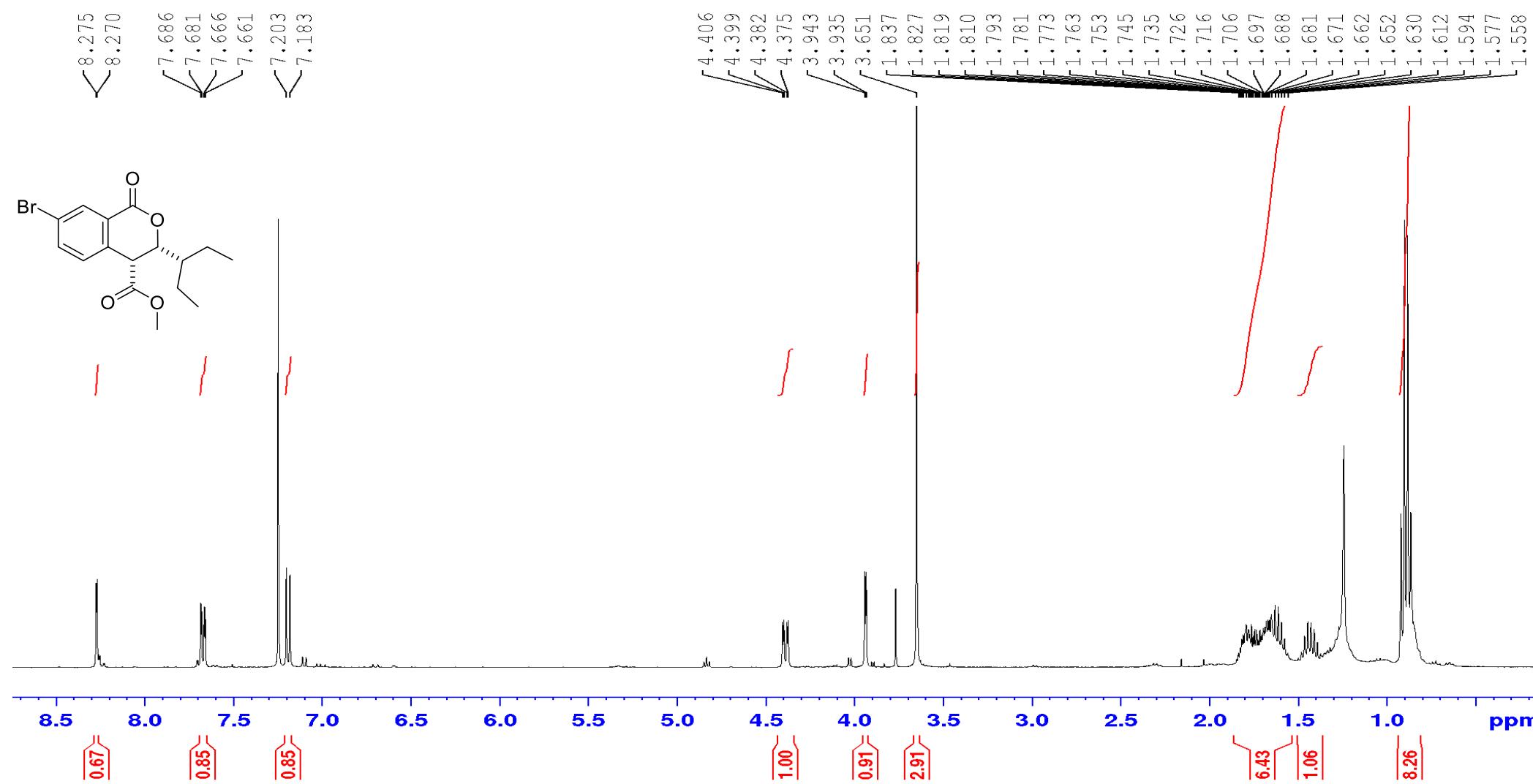
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-51



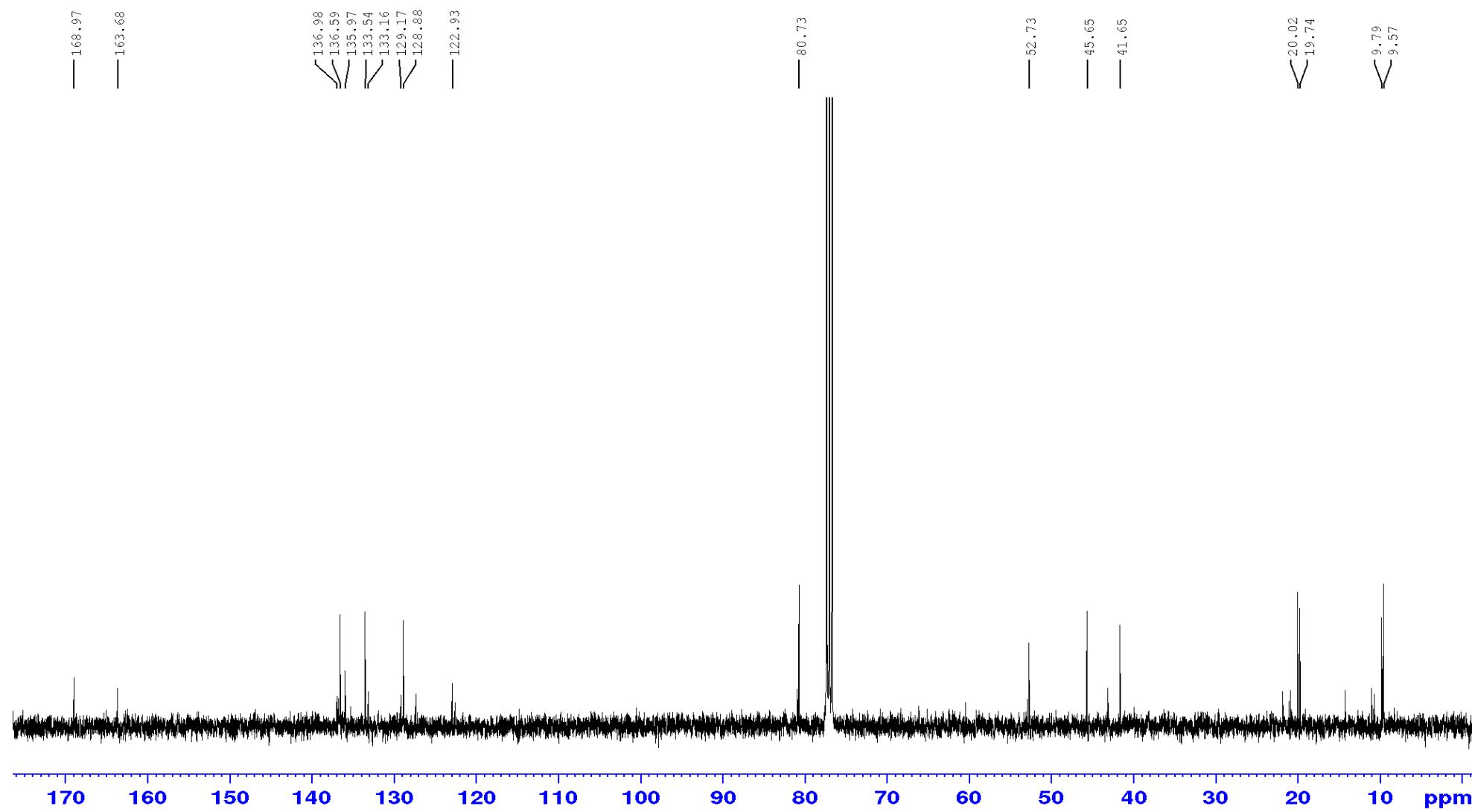
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-51



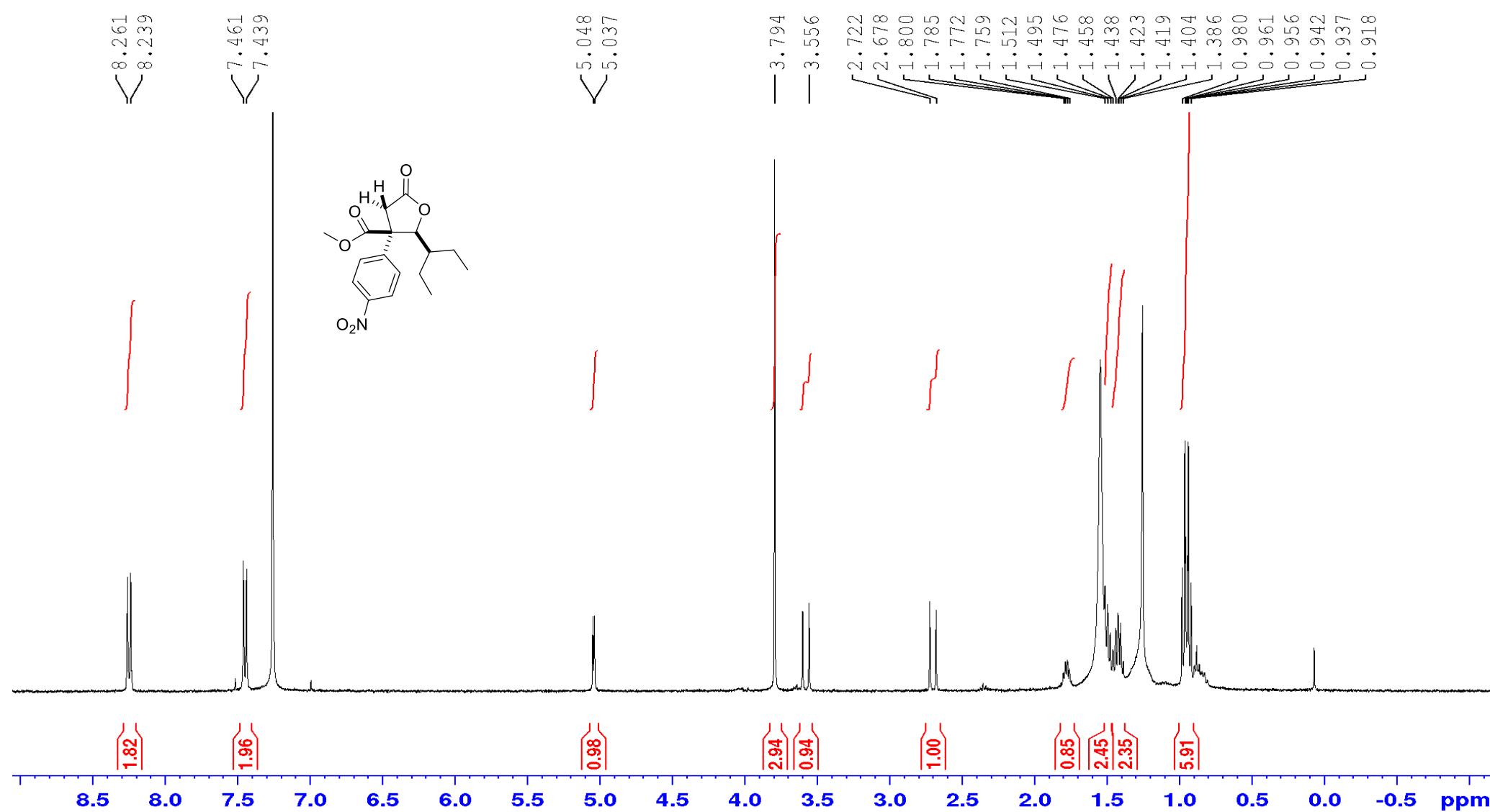
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-54



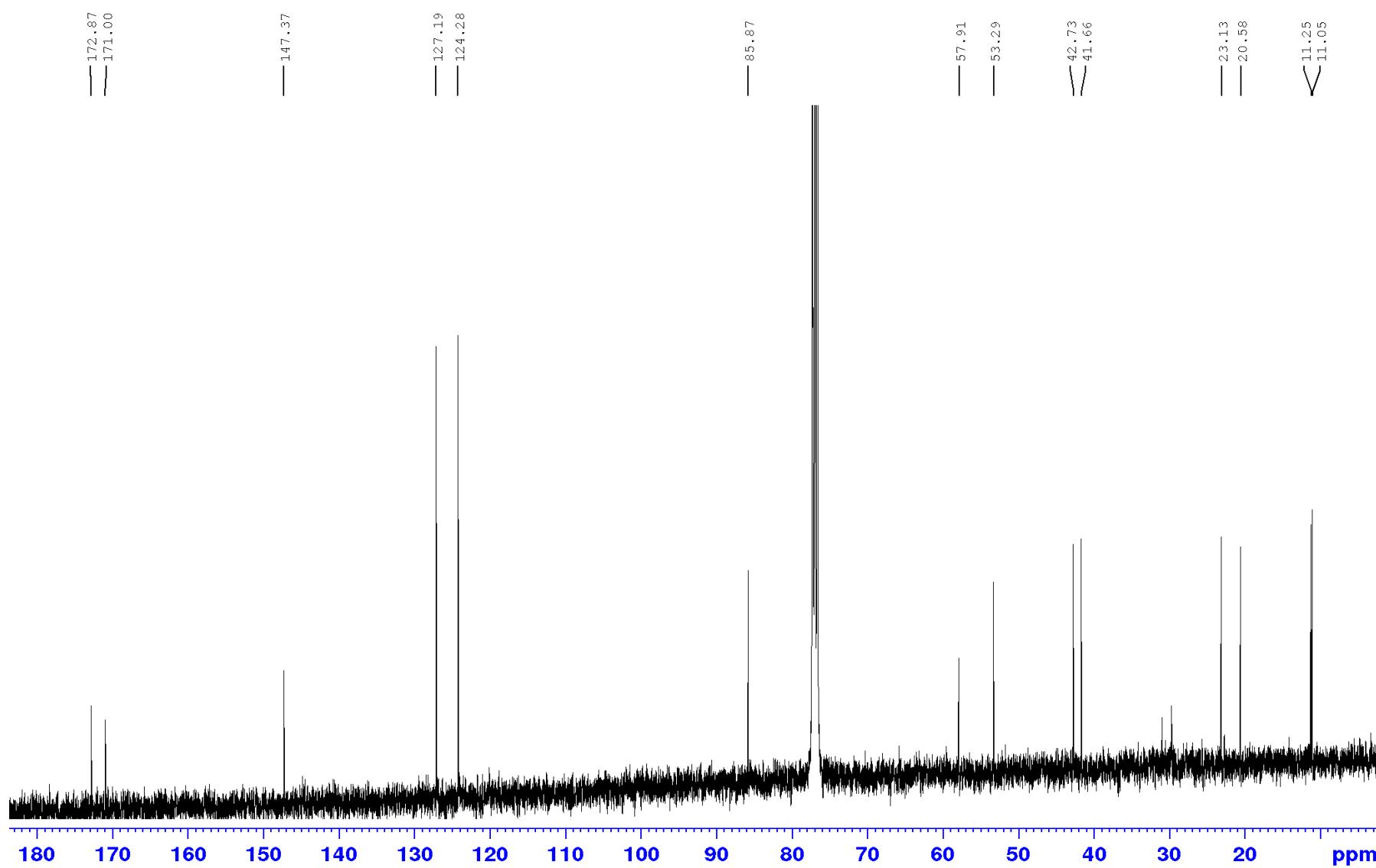
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-54



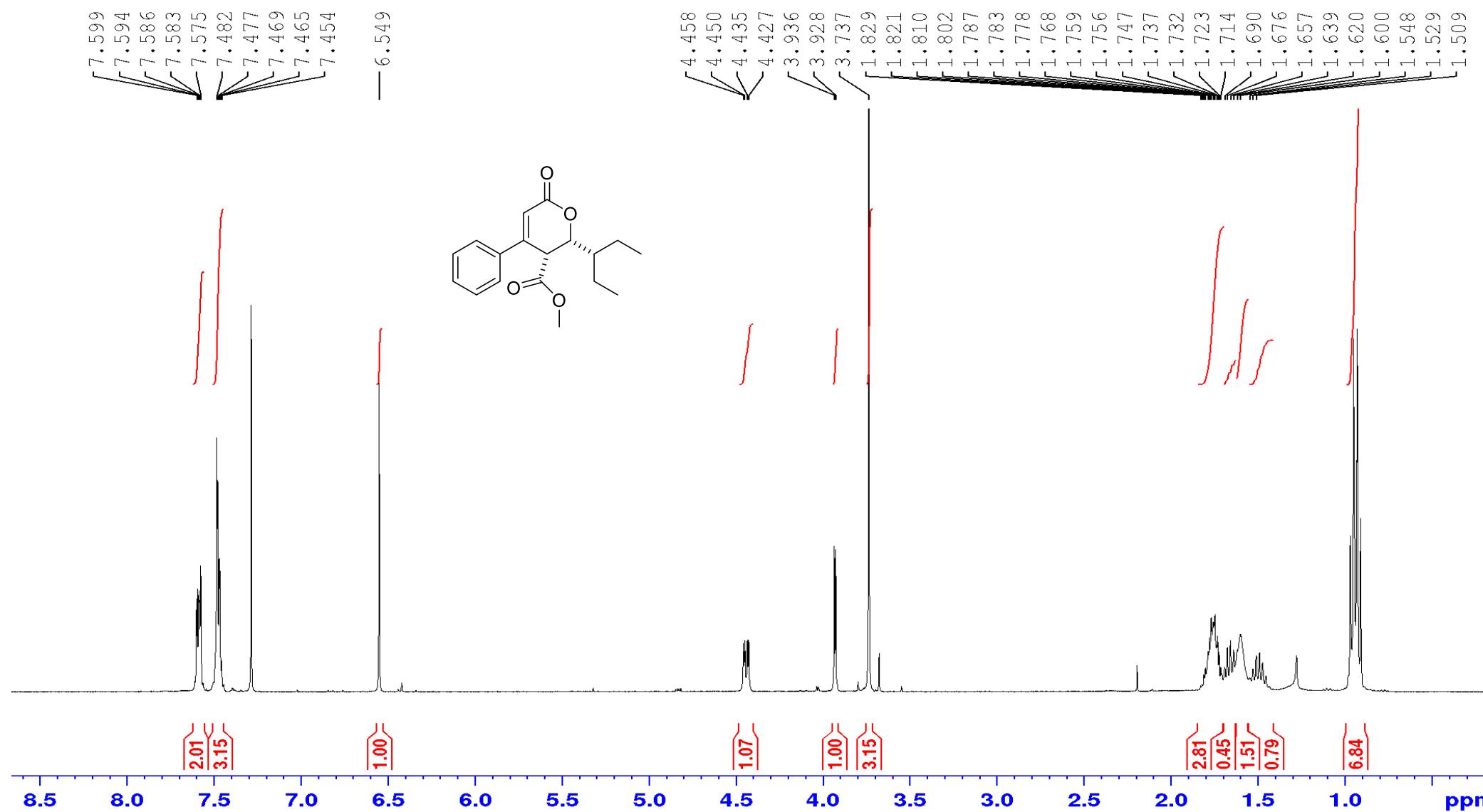
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-56



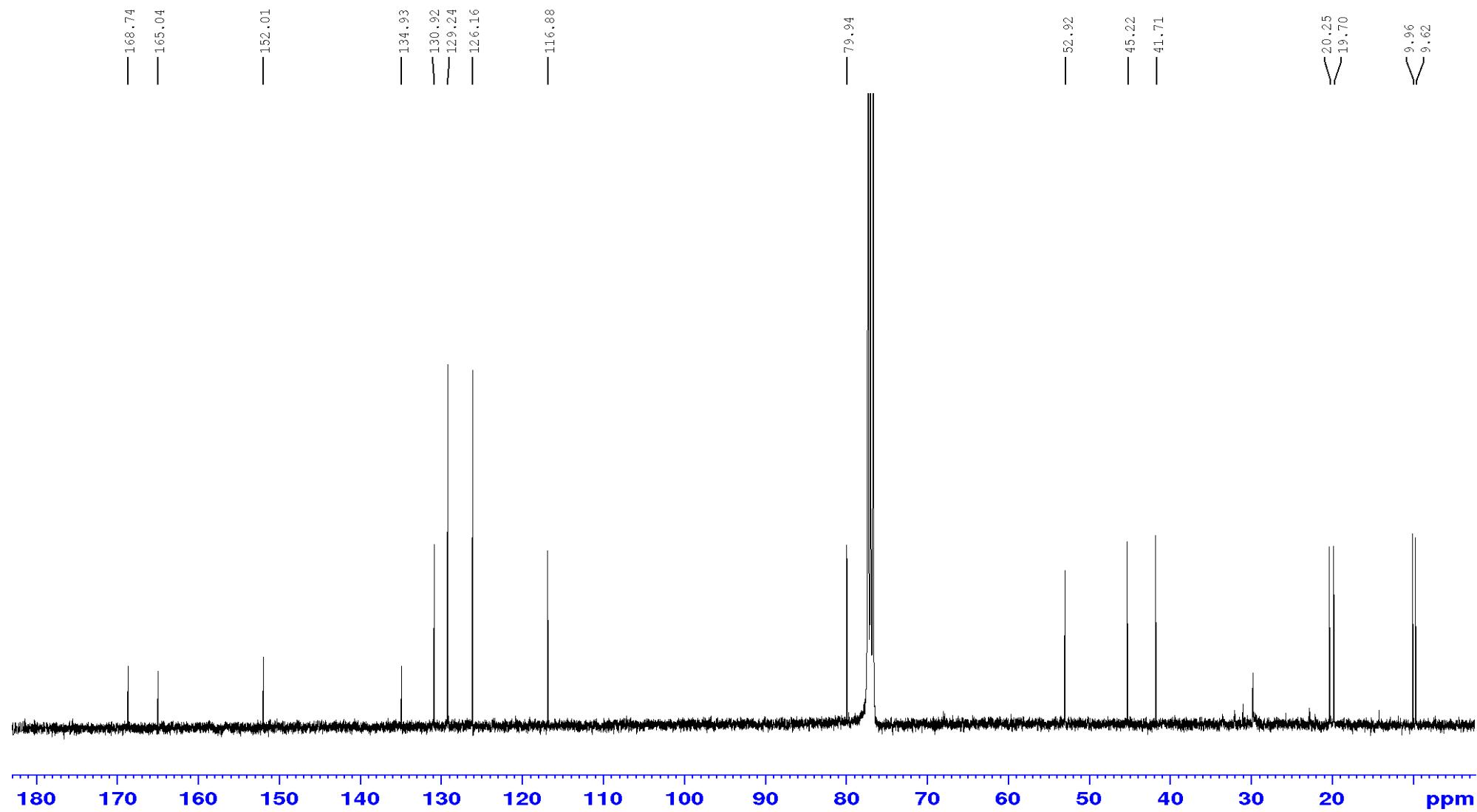
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-56



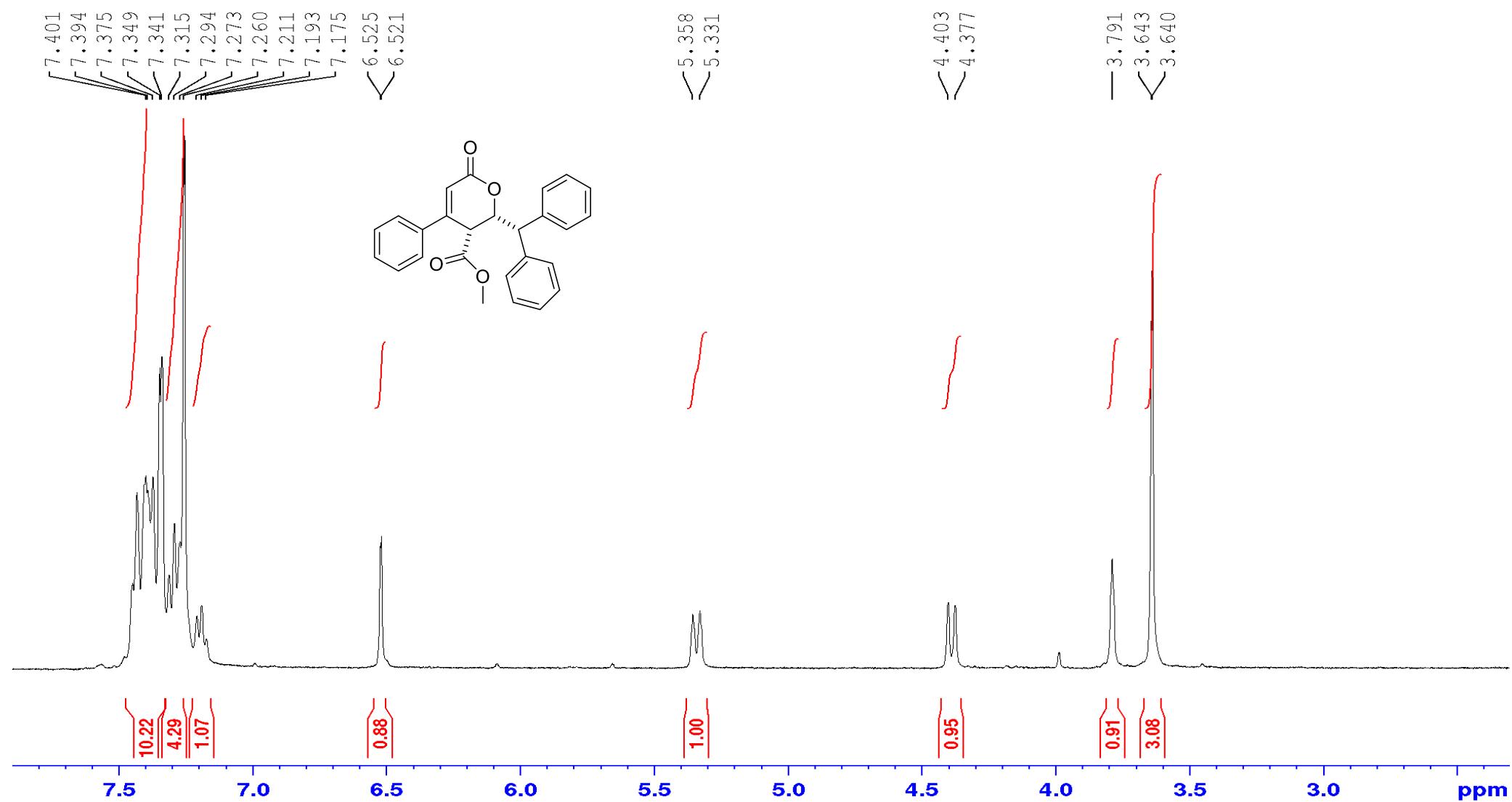
¹H NMR (400 MHz, CDCl₃) spectra of *cis*-58



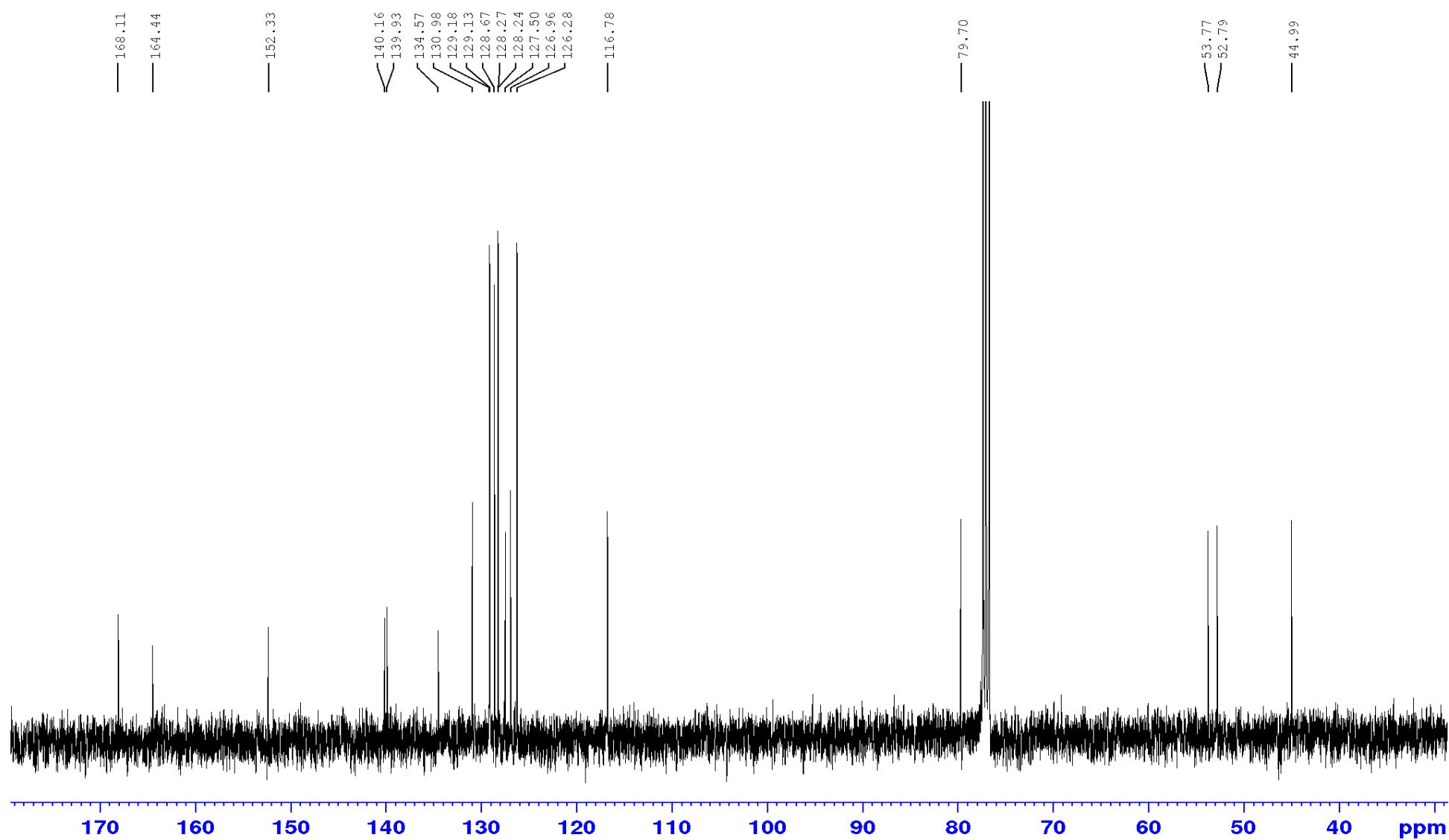
¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-58



¹H NMR (400 MHz, CDCl₃) spectra of *cis*-60



¹³C NMR (100 MHz, CDCl₃) spectra of *cis*-60



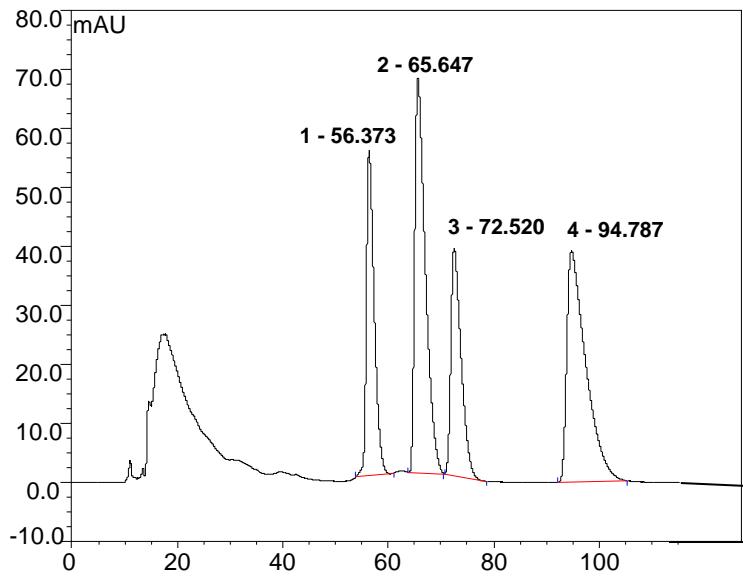
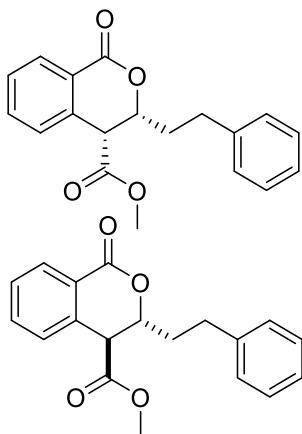
2 HPLC chromatograms

Compound 15a and 15b (racemic)

Chiralcel OJH (4.6 mm x 25 cm), hexane/IPA: 70:30, 0.3 mL min⁻¹, RT, UV detection at 221 nm

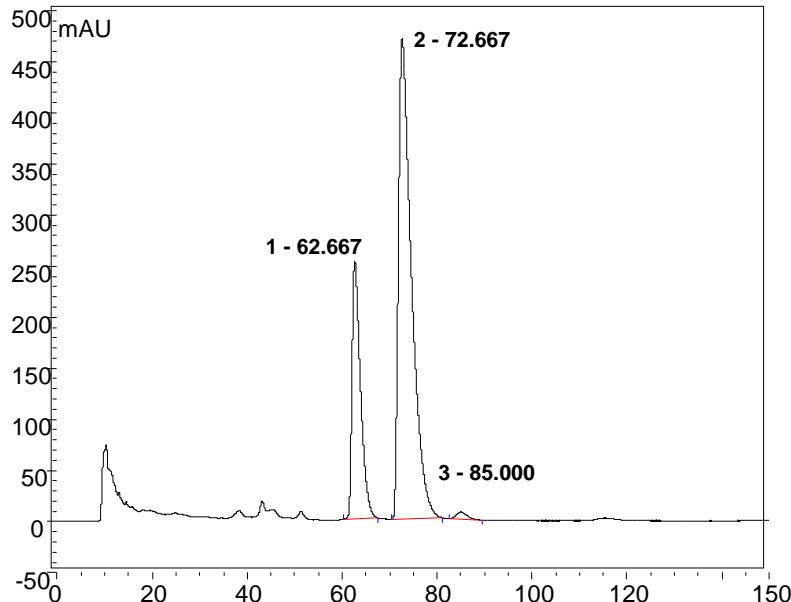
No.	Ret.Time	Rel.Area
	min	%
1	56.37	18.35
2	65.65	31.28
3	72.52	17.32
4	94.78	32.55
Total:		100.0

trans-15
cis-15
trans-15
cis-15



No.	Ret.Time	Rel.Area
	min	%
1	62.66	30.84
2	72.66	67.74
3	85.00	1.36
Total:		100.0

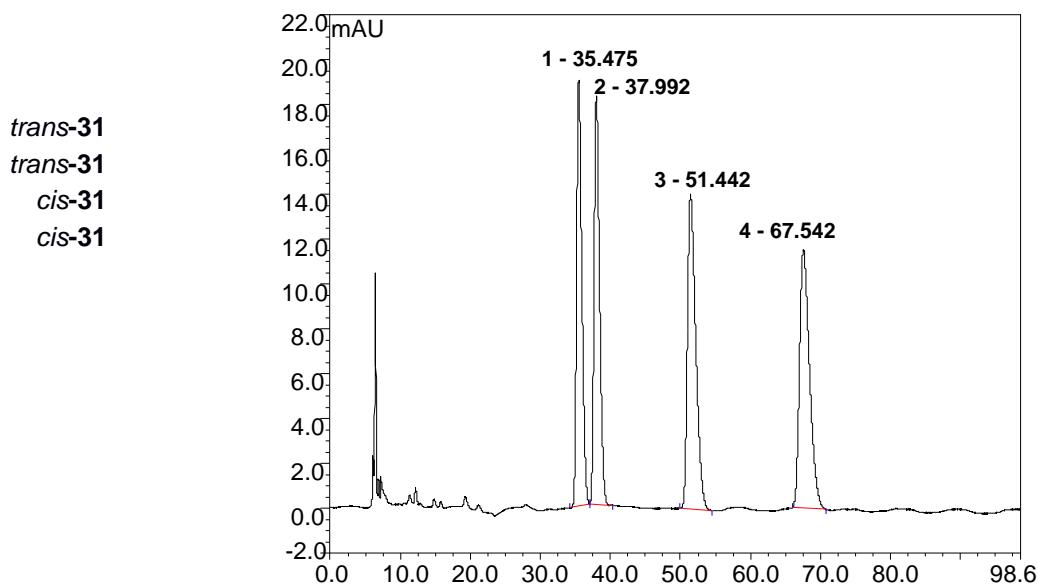
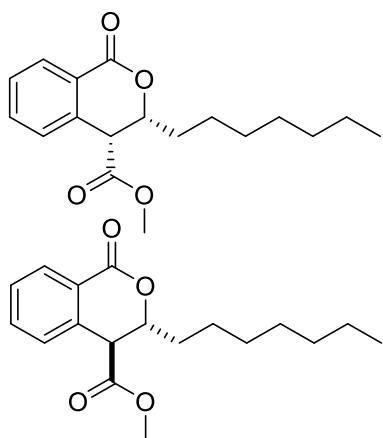
trans-15
cis-15
trans-15



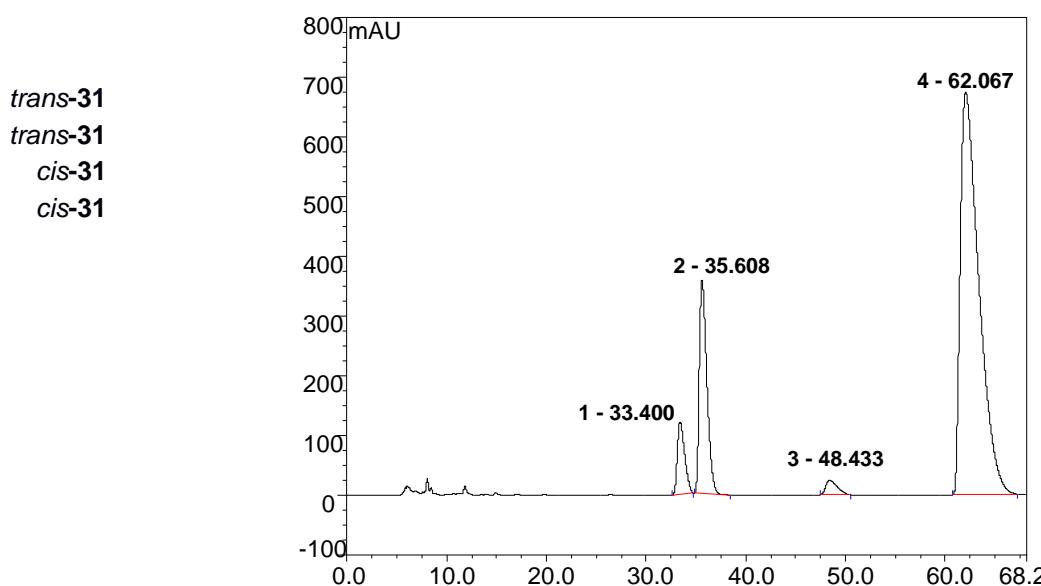
Compound 31 (racemic)

Chiralcel IA (4.6 mm x 25 cm), hexane/IPA: 98/2, 0.5 mL min⁻¹, RT, UV detection at 221 nm

No.	Ret.Time	Rel.Area
	min	%
1	35.47	23.01
2	37.99	23.04
3	51.42	27.08
4	67.54	26.97
Total:		100.0



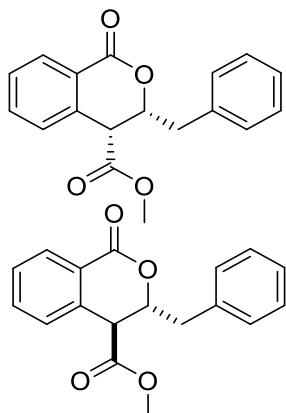
No.	Ret.Time	Rel.Area
	min	%
1	33.40	5.42
2	35.60	16.55
3	48.43	1.69
4	62.06	76.34
Total:		100.0



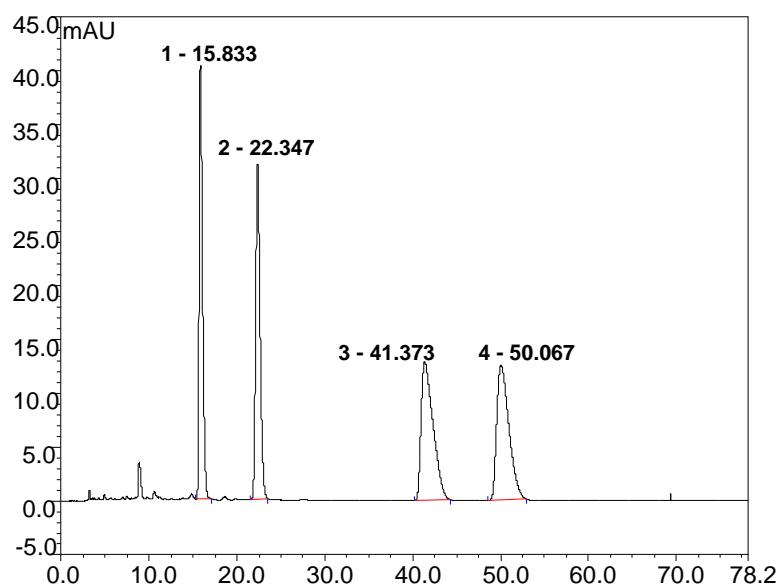
Compound 32 (racemic)

Chiralcel IA (4.6 mm x 25 cm), hexane/IPA:
90/10, 1.0 mL min⁻¹, RT, UV detection at 254 nm

No.	Ret.Time	Rel.Area
	min	%
1	15.83	23.51
2	22.34	23.53
3	41.37	26.52
4	50.06	26.44
Total:		100.0

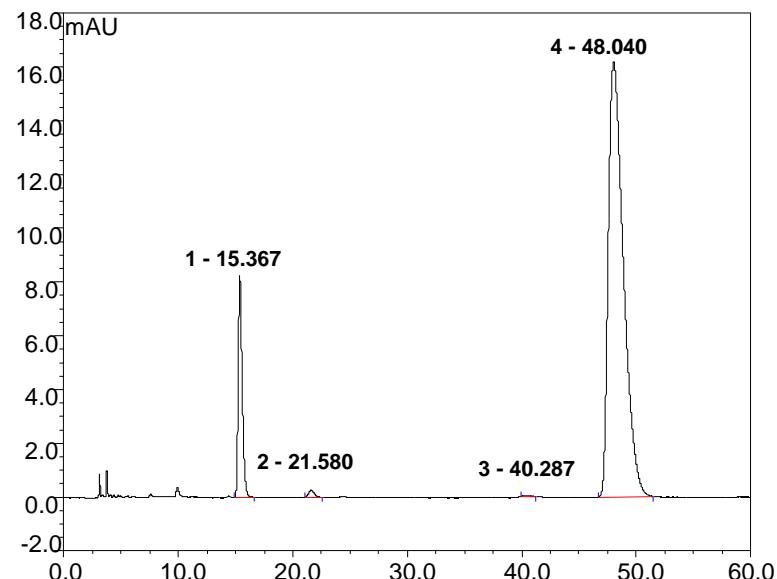


trans-32
cis-32
cis-32



No.	Ret.Time	Rel.Area
	min	%
1	15.36	17.93
2	21.58	0.38
3	40.28	0.30
4	48.04	81.39
Total:		100.0

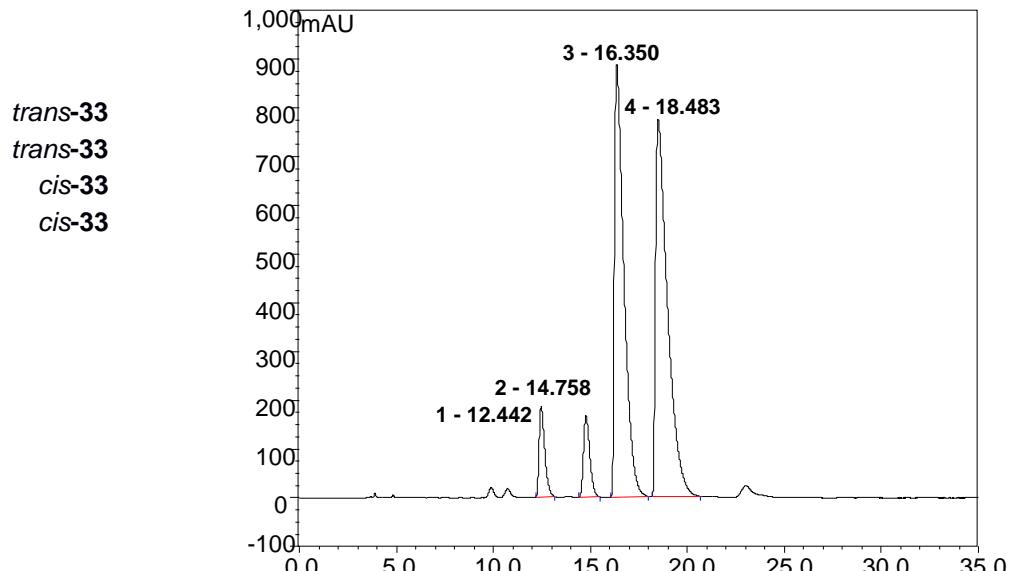
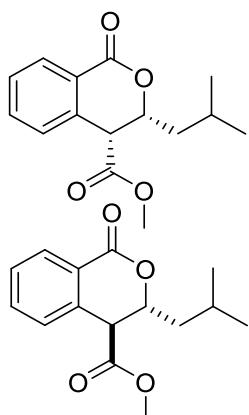
trans-32
cis-32
cis-32



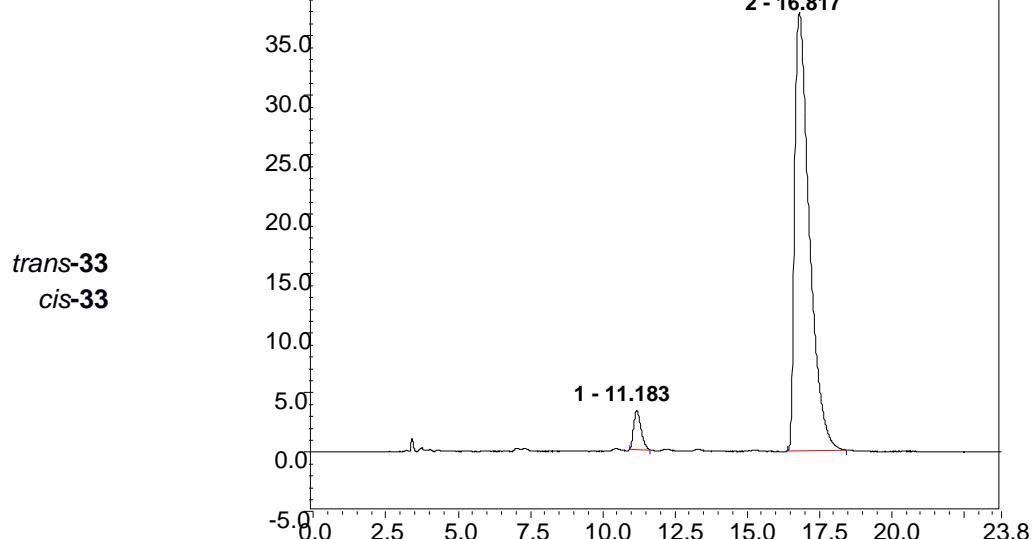
Compound 33 (racemic)

Chiralcel ODH (4.6 mm x 25 cm), hexane/IPA: 95/5, 1.0 mL min⁻¹, RT, UV detection at 221 nm

No.	Ret.Time	Rel.Area
	min	%
1	12.44	5.32
2	14.75	5.29
3	16.35	42.41
4	18.48	46.98
Total:		100.0



No.	Ret.Time	Rel.Area
	min	%
1	11.18	4.32
2	16.81	5.29
Total:		100.0

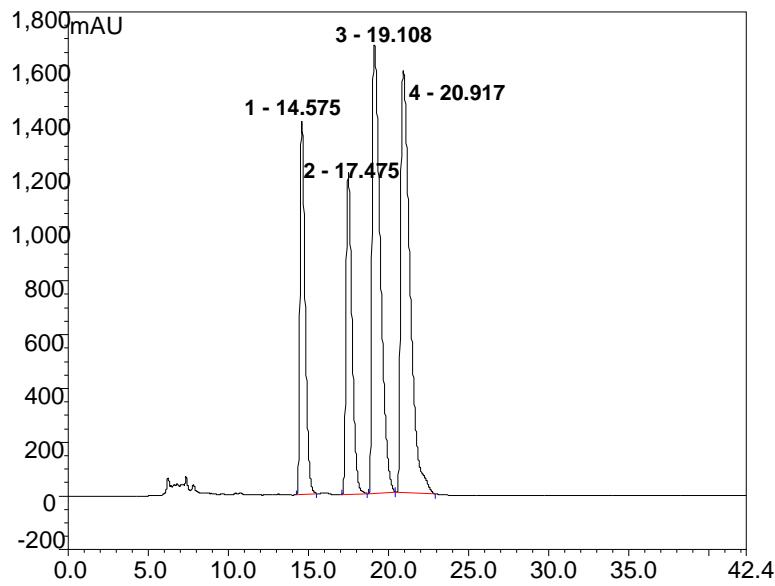
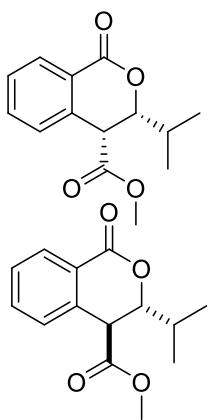


Compound 34 (racemic)

Chiralcel ODH (4.6 mm x 25 cm), hexane/IPA: 85/15, 0.5 L min⁻¹, RT, UV detection at 221 nm

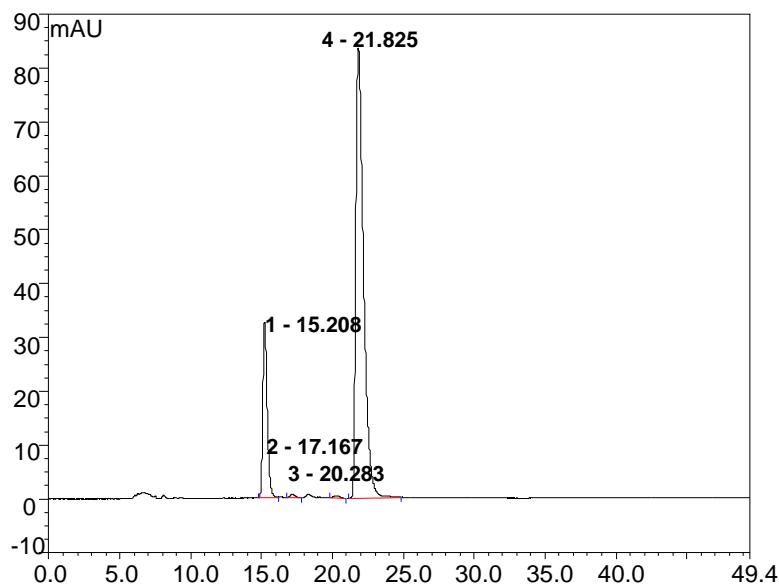
No.	Ret.Time	Rel.Area
	min	%
1	14.57	16.57
2	17.47	16.83
3	19.10	32.18
4	20.91	34.41
Total:		100.0

trans-34
trans-34
cis-34
cis-34



No.	Ret.Time	Rel.Area
	min	%
1	15.20	17.93
2	17.16	0.38
3	20.28	0.30
4	21.82	81.39
Total:		100.0

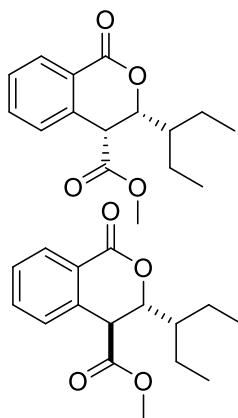
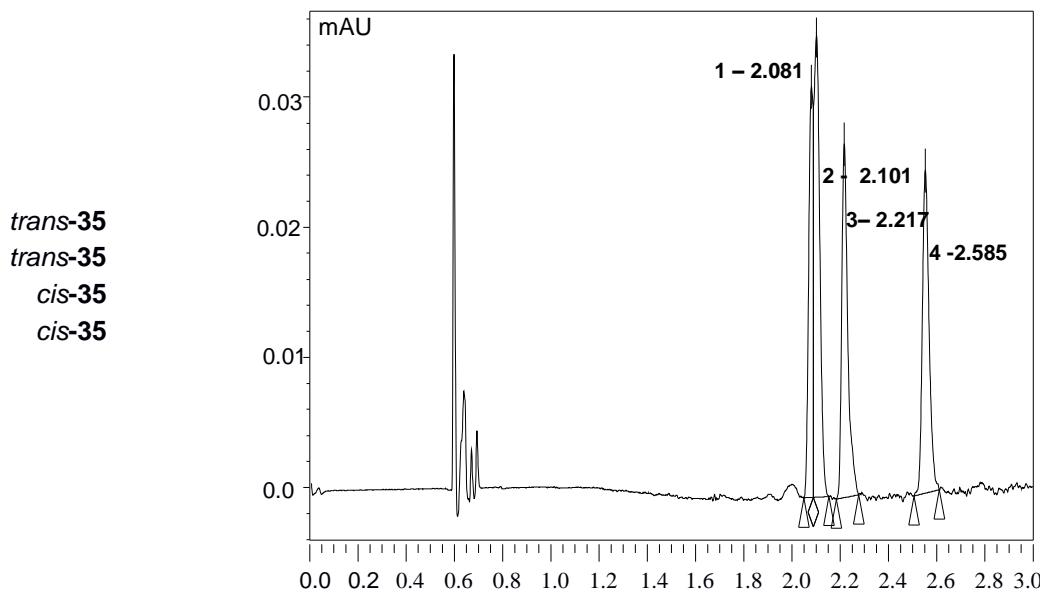
trans-34
trans-34
cis-34
cis-34



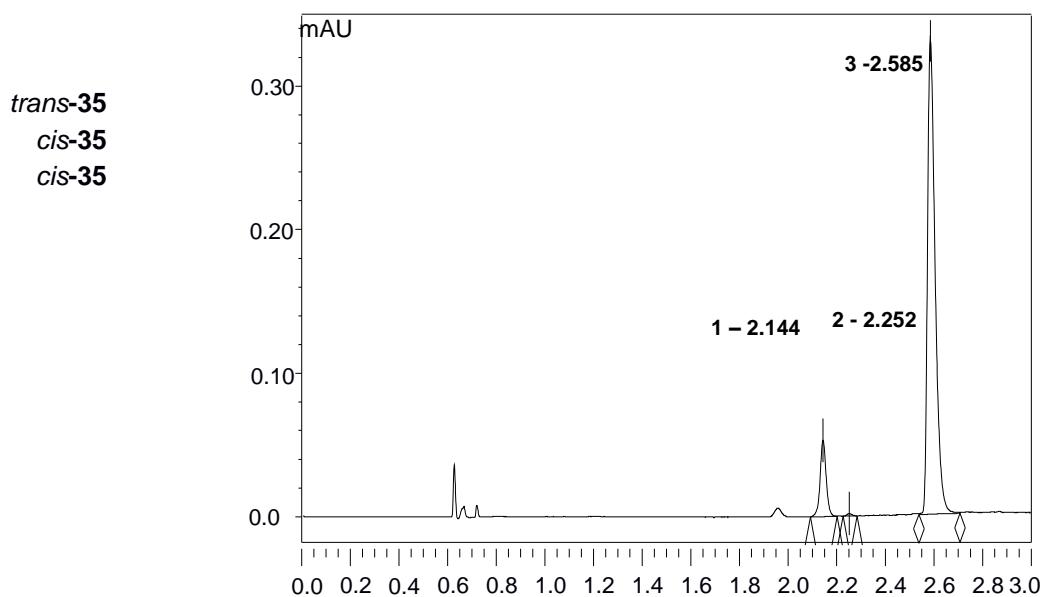
Compound 35 (racemic)

CSP-HPLC analysis. ACQUITY UPC², Trefoil AMY1, 2.5μm (3.0 x 150mm). ABPR: 1500 (psi). A (CO₂) = 97%/B (Ethanol/ACN/IPA 1:1:1, v:v:v) = 3%, 1.2 mL min⁻¹, 30 °C, UV detection at 254 nm

No.	Ret.Time	Rel.Area
	min	%
1	2.08	20.01
2	2.10	31.14
3	2.21	24.28
4	2.58	24.57
Total:		100.0



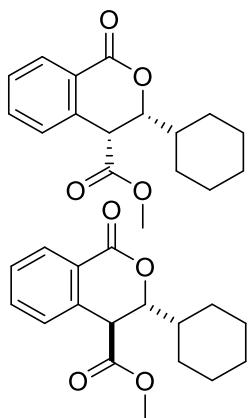
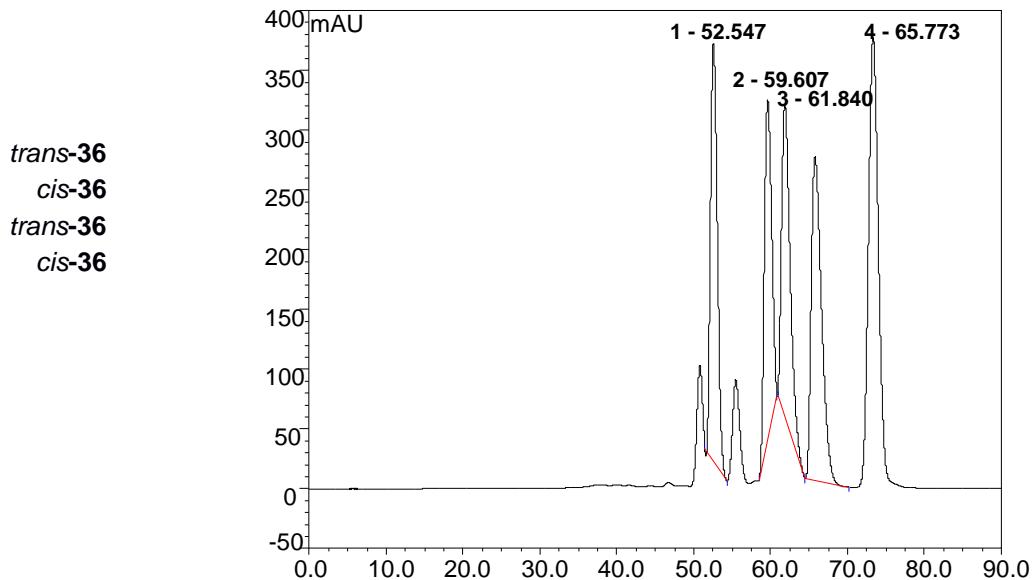
No.	Ret.Time	Rel.Area
	min	%
1	2.14	11.24
2	2.25	0.29
3	2.58	88.47
Total:		100.0



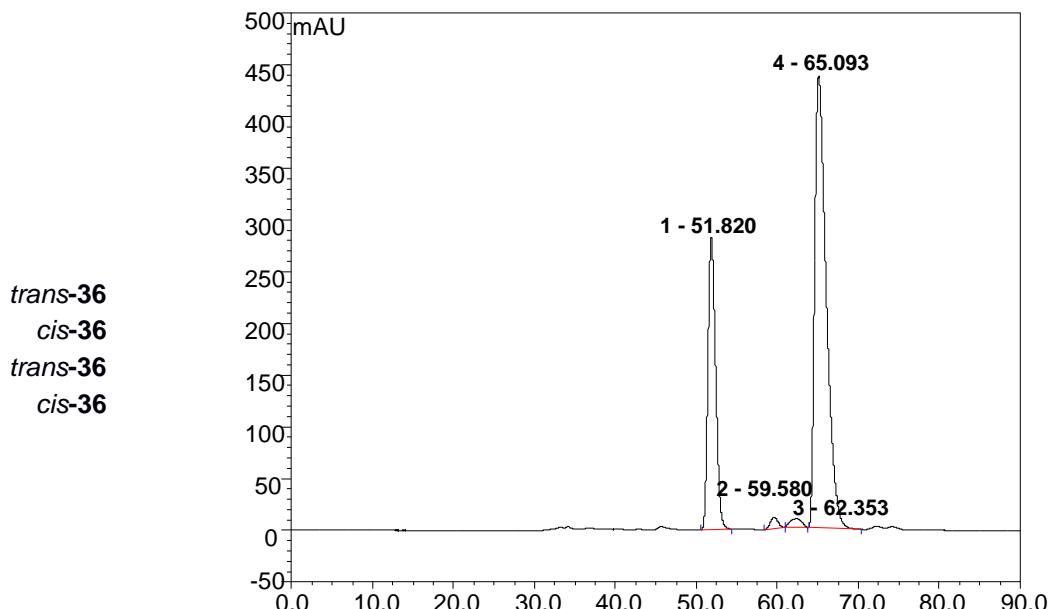
Compound 36 (racemic)

Chiralcel ODH (4.6 mm x 25 cm), hexane/IPA: 60/40, 1.0 mL min⁻¹, RT, UV detection at 254 nm

No.	Ret.Time	Rel.Area
	min	%
1	52.54	25.27
2	59.60	21.81
3	61.84	23.58
4	65.77	29.35
Total:		100.0



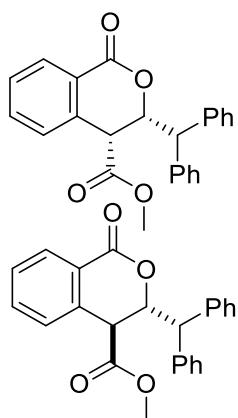
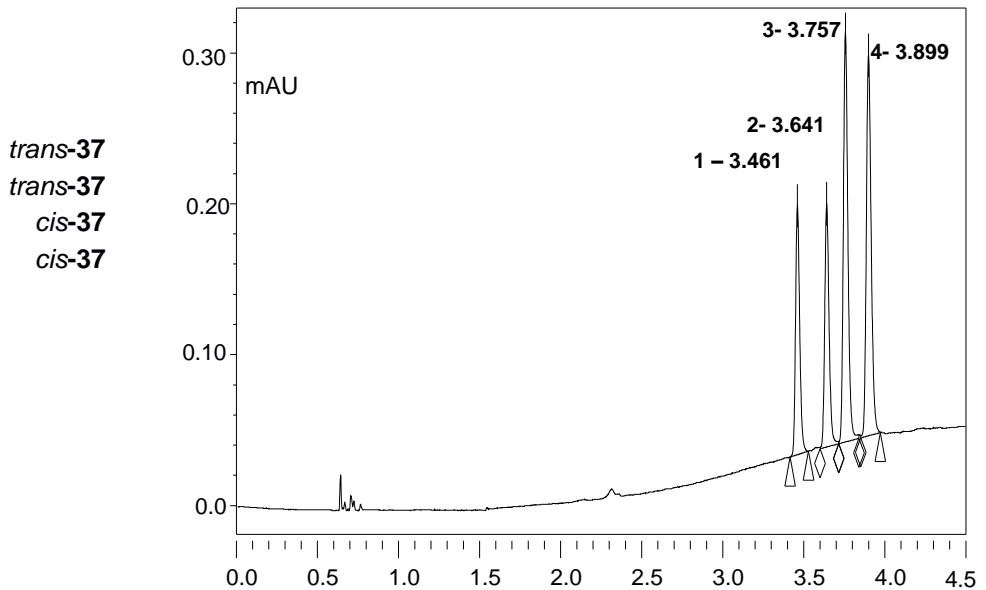
No.	Ret.Time	Rel.Area
	min	%
1	51.82	29.17
2	59.58	1.10
3	62.35	1.34
4	65.09	68.39
Total:		100.0



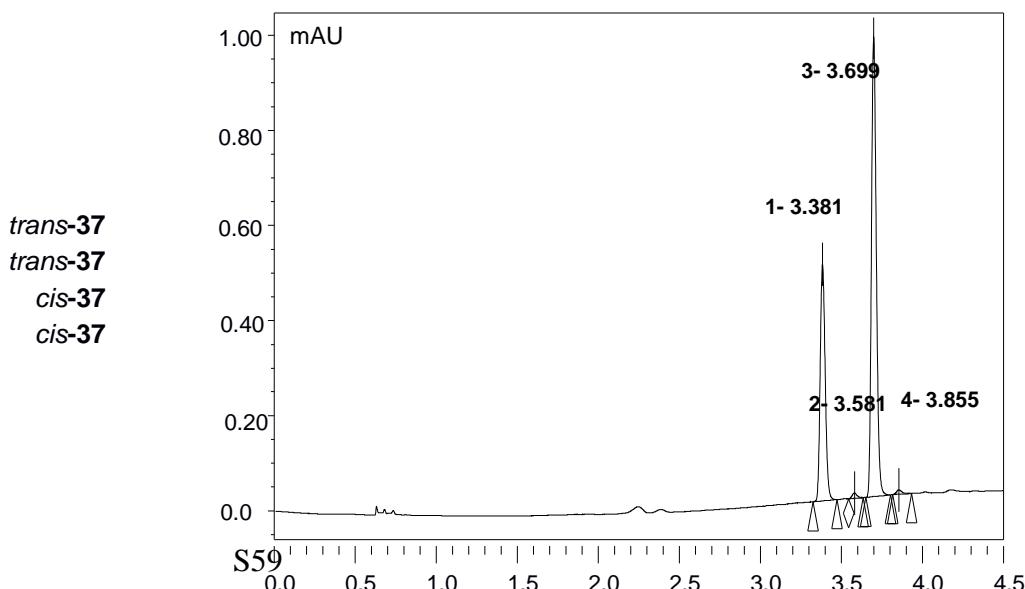
Compound 37 (racemic)

CSP-HPLC analysis. ACQUITY UPC², Trefoil AMY1, 2.5μm (3.0 x 150mm). ABPR: 1500 (psi). A (CO₂) = 97%/B (Ethanol/ACN/IPA 1:1:1, v:v:v) = 3%, 1.2 mL min⁻¹, 30 °C, UV detection at 254 nm

No.	Ret.Time	Rel.Area
	min	%
1	3.46	17.86
2	3.64	18.20
3	3.75	32.08
4	3.89	31.86
Total:		100.0



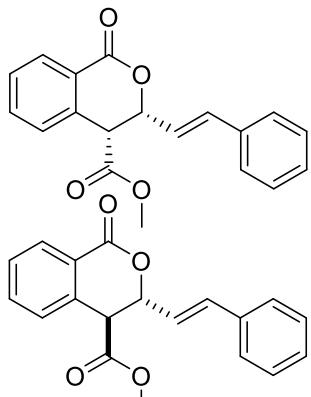
No.	Ret.Time	Rel.Area
	min	%
1	3.38	34.10
2	3.58	0.77
3	3.69	64.40
4	3.85	0.73
Total:		100.0



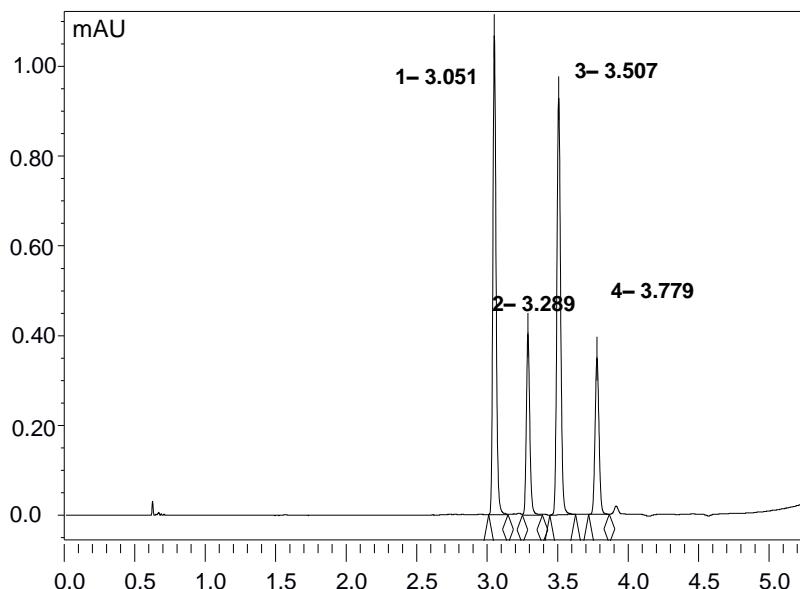
Compound 38 (racemic)

CSP-HPLC analysis. ACQUITY UPC², Trefoil AMY1, 2.5μm (3.0 x 150mm). ABPR: 1500 (psi). A (CO₂) = 97%/B (Ethanol/ACN/IPA 1:1:1, v:v:v) = 3%, 1.2 mL min⁻¹, 30 °C, UV detection at 254 nm

No.	Ret.Time	Rel.Area
	min	%
1	3.05	35.29
2	3.28	14.37
3	3.50	36.07
4	3.77	14.27
Total:		100.0

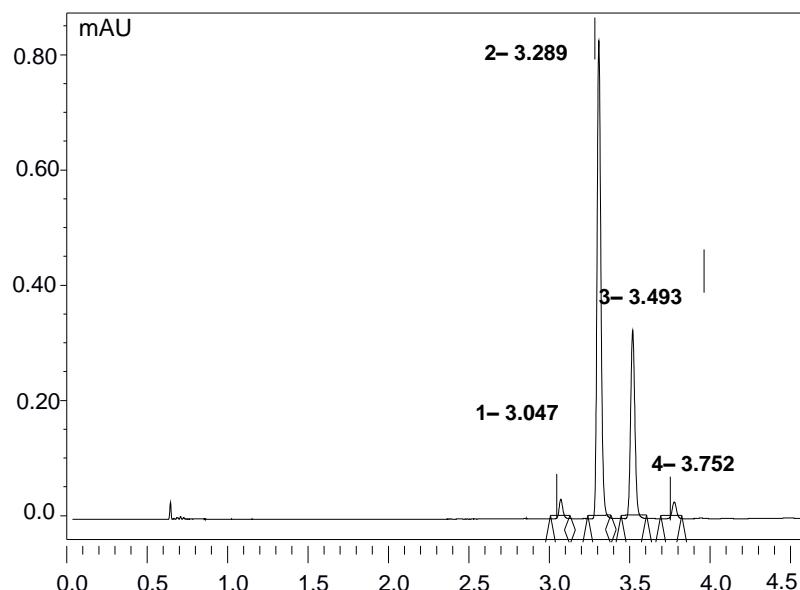


trans-38
cis-38
trans-38
cis-38



No.	Ret.Time	Rel.Area
	min	%
1	3.04	2.59
2	3.28	65.79
3	3.49	29.01
4	3.75	2.61
Total:		100.0

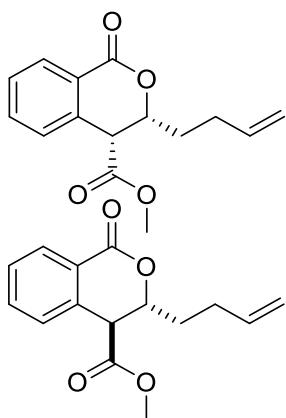
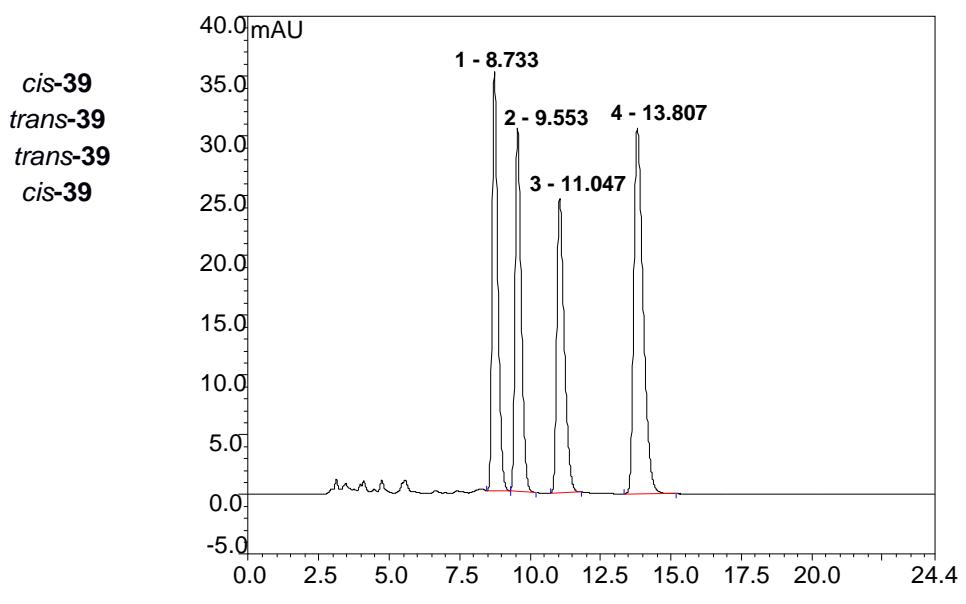
trans-38
cis-38
trans-38
cis-38



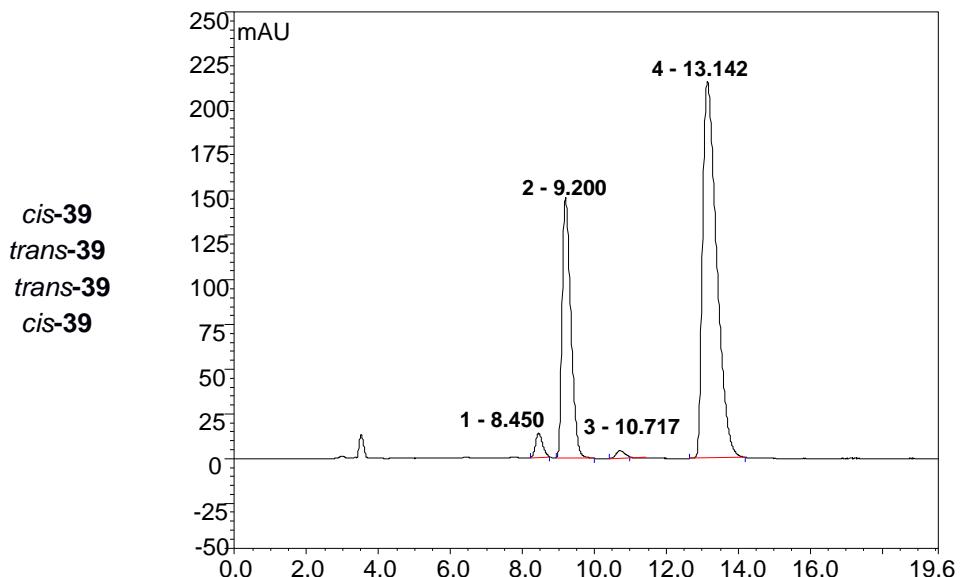
Compound 39 (racemic)

Chiralcel IA (4.6 mm x 25 cm), hexane/IPA: 90/10, 1.0 mL min⁻¹, RT, UV detection at 254

No.	Ret.Time	Rel.Area
	min	%
1	8.73	27.11
2	9.55	24.79
3	11.04	19.15
4	13.80	28.59
Total:		100.0



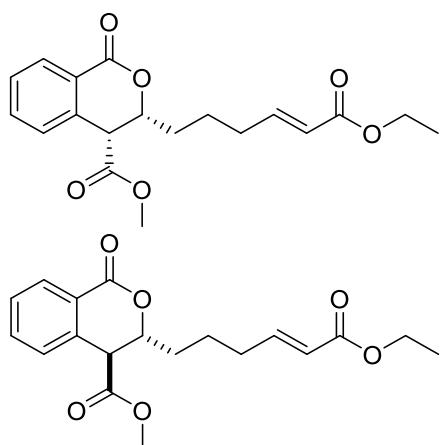
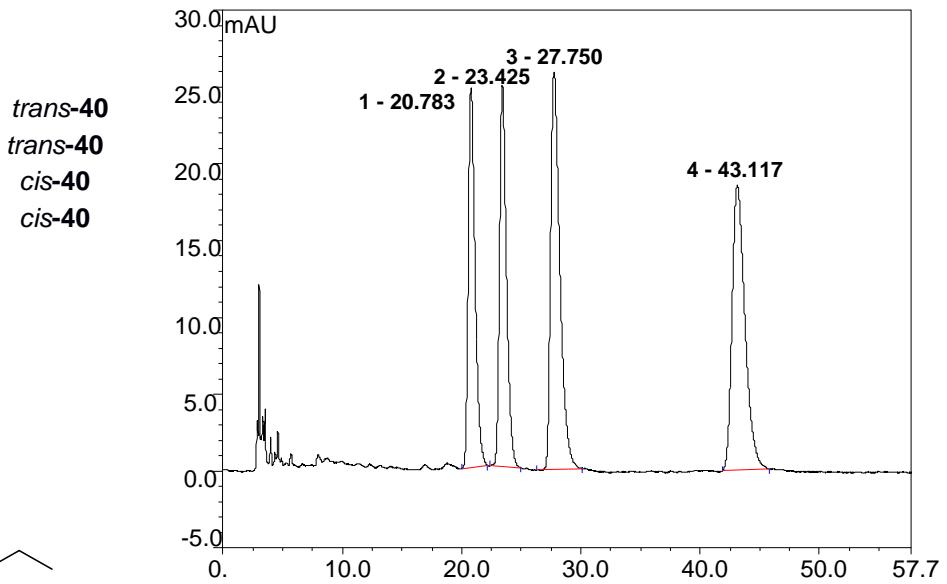
No.	Ret.Time	Rel.Area
	min	%
1	8.45	2.17
2	9.20	29.04
3	10.71	0.70
4	13.14	68.09
Total:		100.0



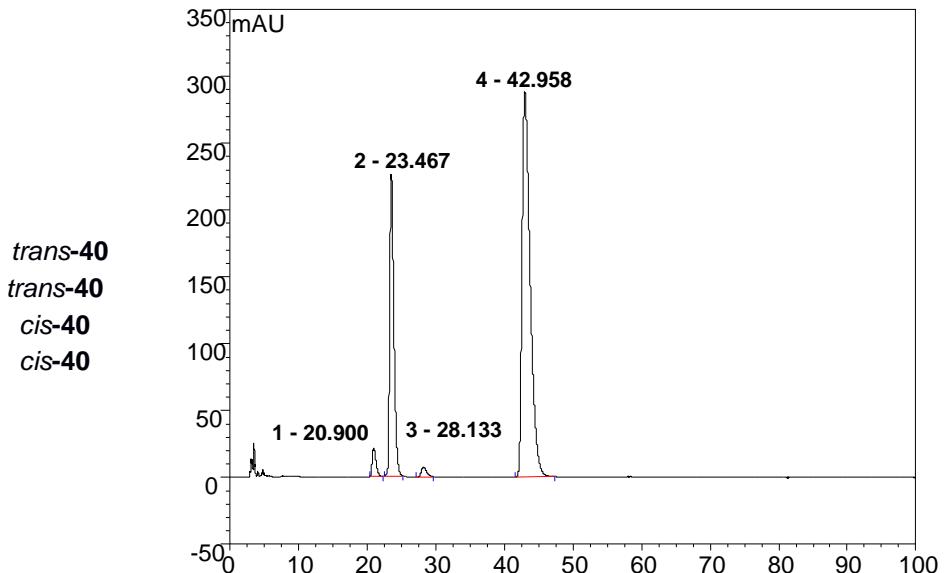
Compound 40 (racemic)

Chiralcel IA (4.6 mm x 25 cm), hexane/IPA: 90/10, 1.0 mL min⁻¹, RT, UV detection at 221 nm

No.	Ret.Time	Rel.Area
	min	%
1	20.78	20.57
2	23.42	20.95
3	27.75	29.30
4	43.17	29.18
Total:		100.0



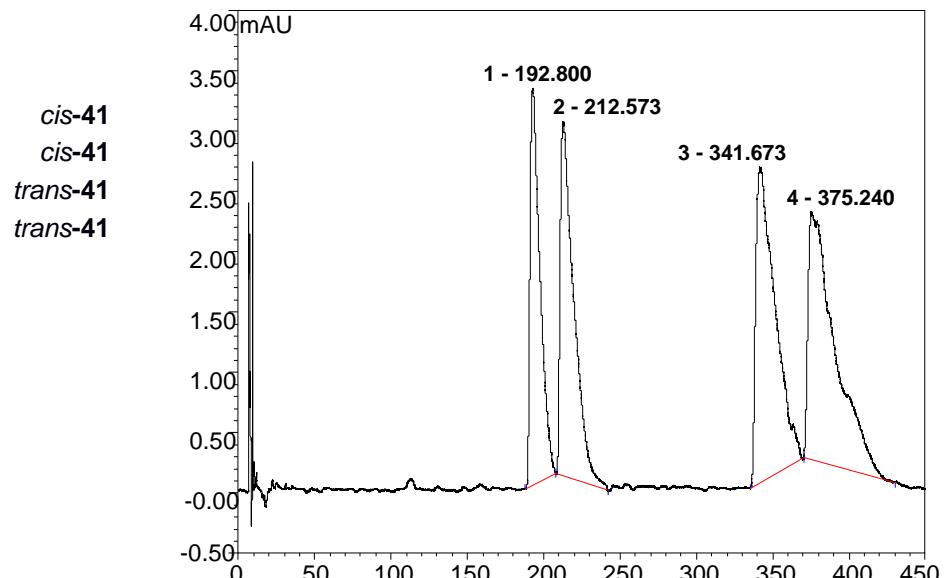
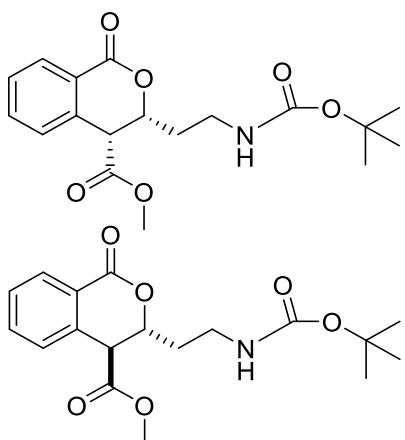
No.	Ret.Time	Rel.Area
	min	%
1	20.90	2.37
2	23.46	27.53
3	28.13	1.16
4	42.95	68.95
Total:		100.0



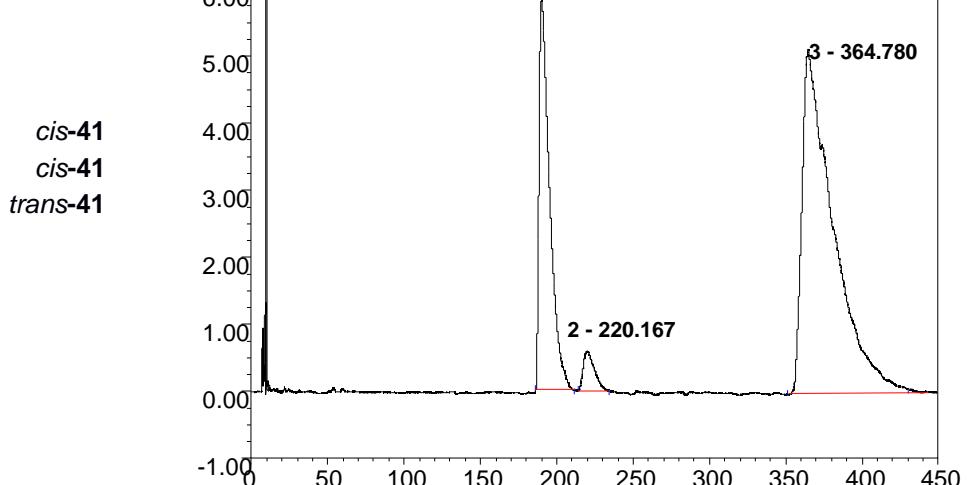
Compound 41 (racemic)

Chiralcel ODH (4.6 mm x 25 cm), hexane/IPA: 98/2, 0.5 mL min⁻¹, RT, UV detection at 254 nm

No.	Ret.Time	Rel.Area
	min	%
1	192.80	18.34
2	212.57	22.31
3	341.63	28.30
4	375.24	31.15
Total:		100.0



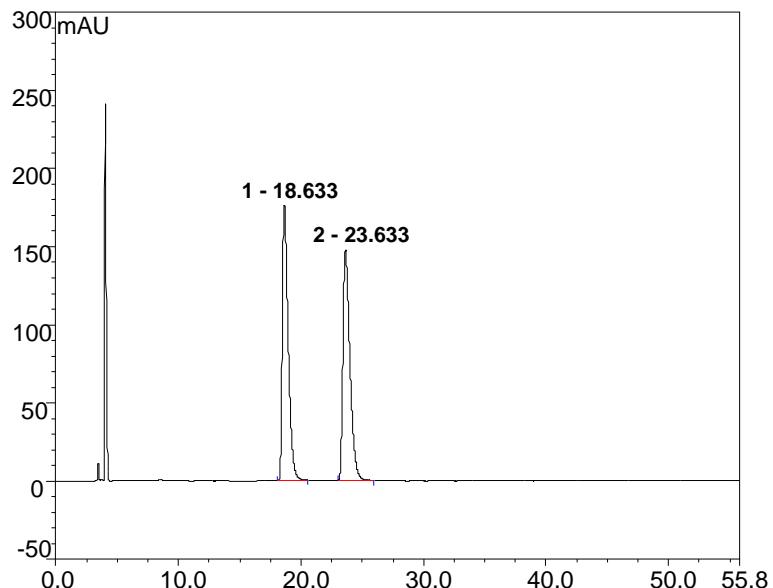
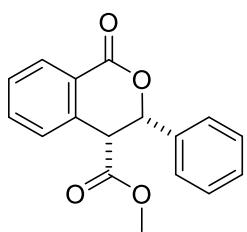
No.	Ret.Time	Rel.Area
	min	%
1	190.08	27.31
2	220.16	2.91
3	364.78	69.68
Total:		100.0



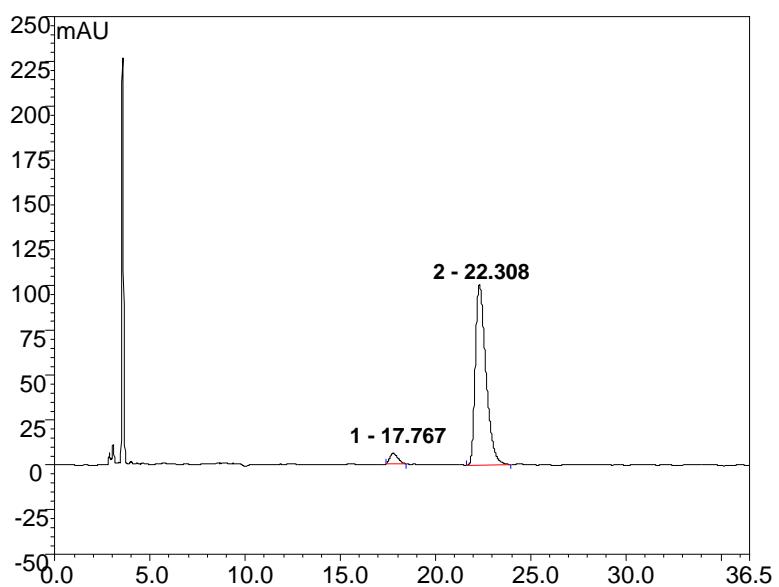
Compound 42 (racemic)

Chiralcel IA (4.6 mm x 25 cm), hexane/IPA: 90/10, 1.0 mL min⁻¹, RT, UV detection at 221 nm.

No.	Ret.Time	Rel.Area
	Min	%
1	18.63	49.9
2	23.63	50.0
Total:		100.00



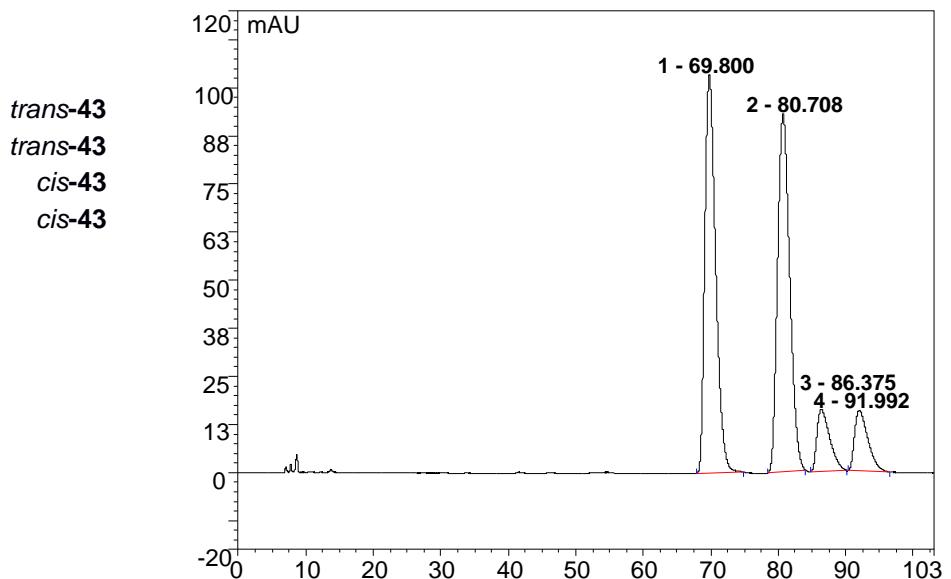
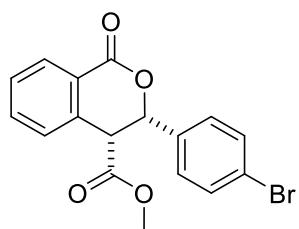
No.	Ret.Time	Rel.Area
	Min	%
1	17.76	4.15
2	22.30	95.85
Total:		100.00



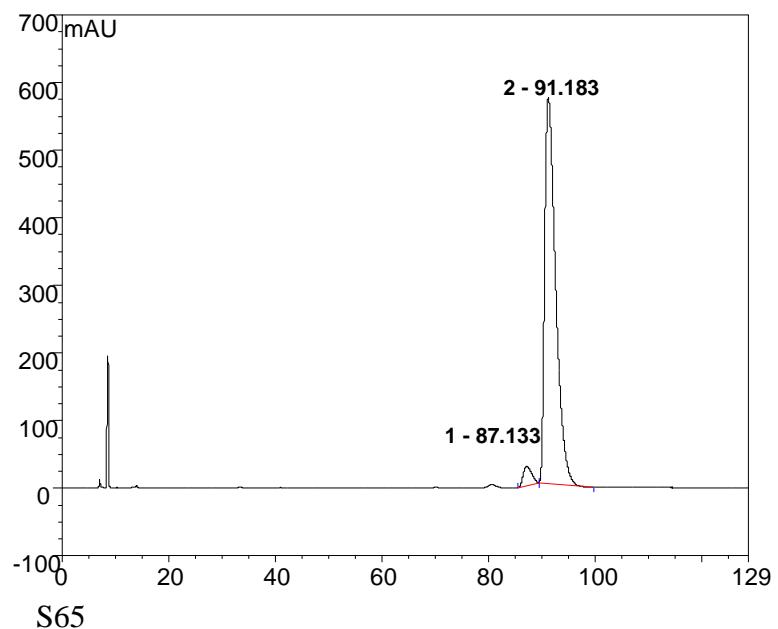
Compound 43 (racemic)

Chiralcel IA (4.6 mm x 25 cm), hexane/IPA: 95/5, 0.5 mL min⁻¹, RT, UV detection at 221 nm.

No.	Ret.Time	Rel.Area
	Min	%
1	69.80	42.01
2	80.70	42.40
3	86.37	7.75
4	91.99	7.84
Total:		100.0



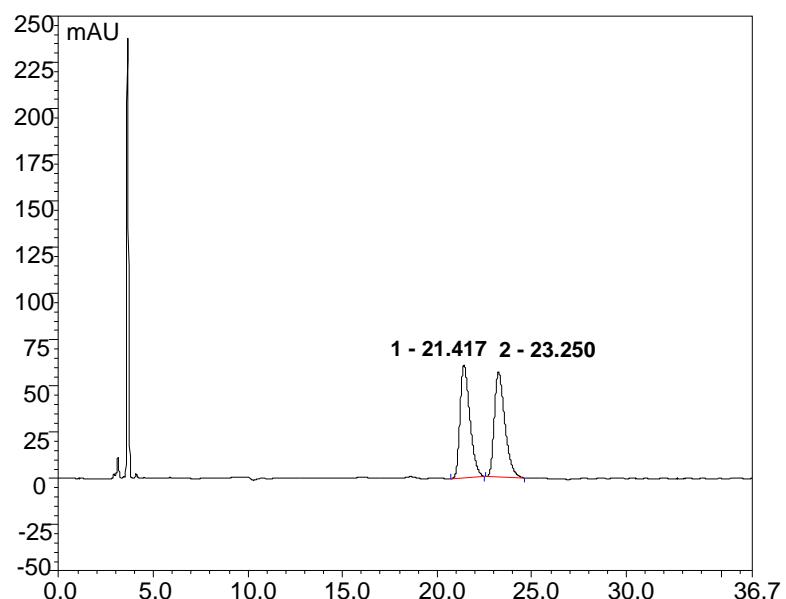
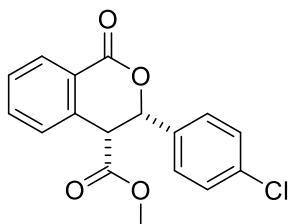
No.	Ret.Time	Rel.Area
	Min	%
1	87.13	3.79
2	91.18	96.21
Total:		100.0



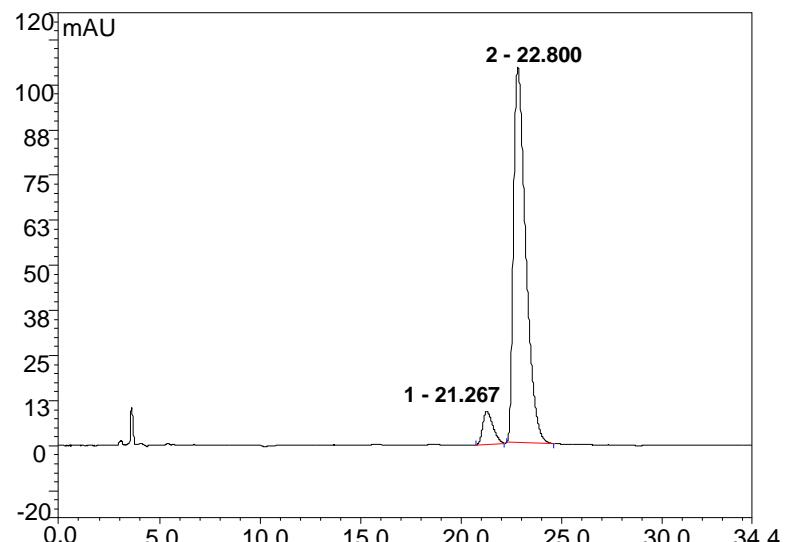
Compound 44 (racemic)

Chiralcel IA (4.6 mm x 25 cm), hexane/IPA: 90/10, 1.0 mL min⁻¹, RT, UV detection at 221 nm.

No.	Ret.Time	Rel.Area
	Min	%
1	21.41	49.54
2	23.25	50.46
Total:		100.0



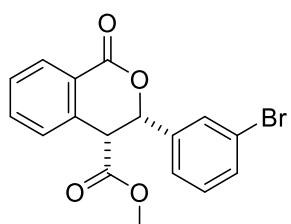
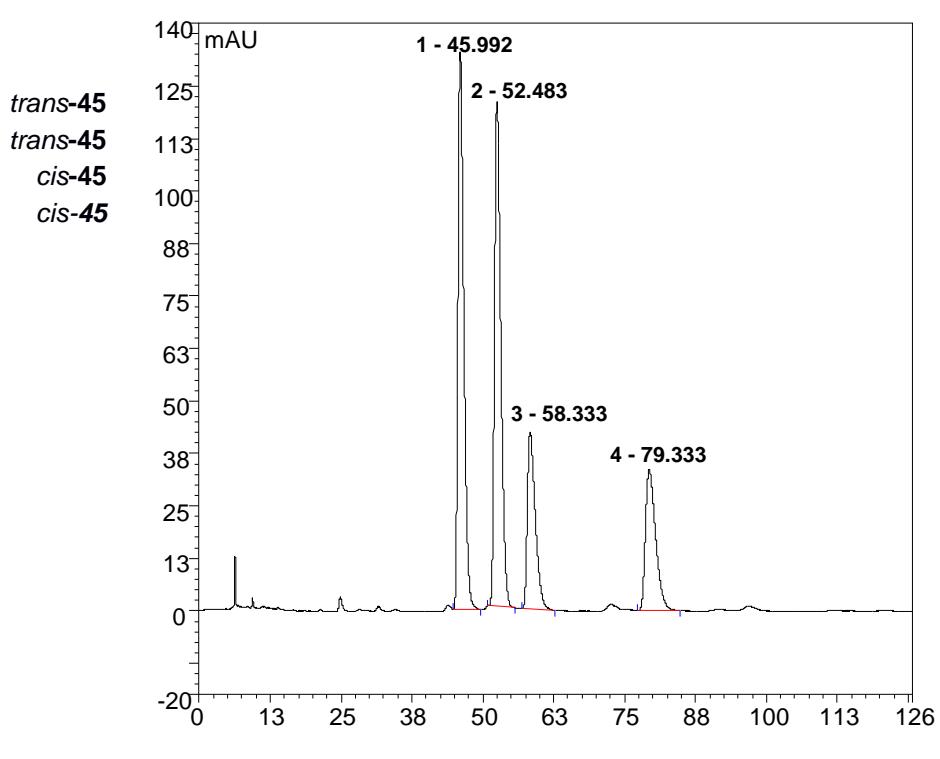
No.	Ret.Time	Rel.Area
	min	%
1	21.26	6.76
2	22.80	93.24
Total:		100.0



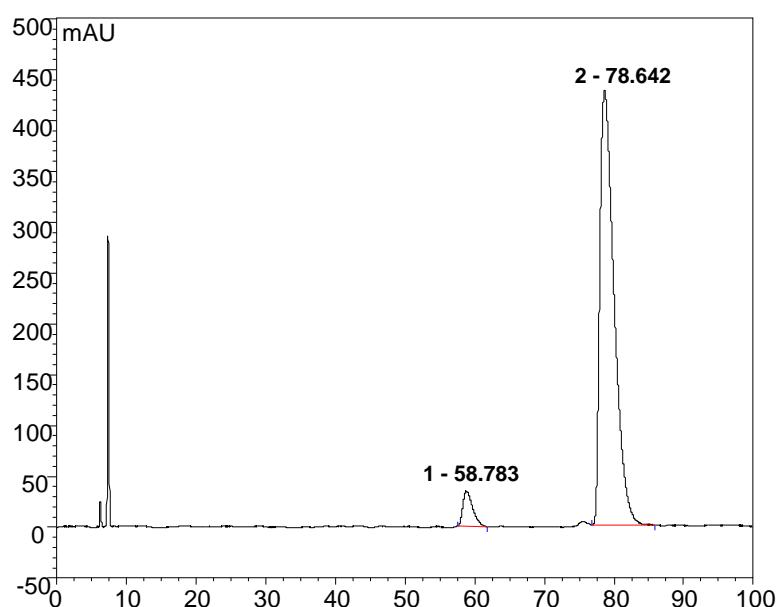
Compound 45 (racemic)

Chiralcel IA (4.6 mm x 25 cm), hexane/IPA: 95/5, 1.0 mL min⁻¹, RT, UV detection at 221 nm

No.	Ret.Time	Rel.Area
	min	%
1	45.99	34.92
2	52.48	34.35
3	58.33	15.16
4	79.33	15.56
Total:		100.0



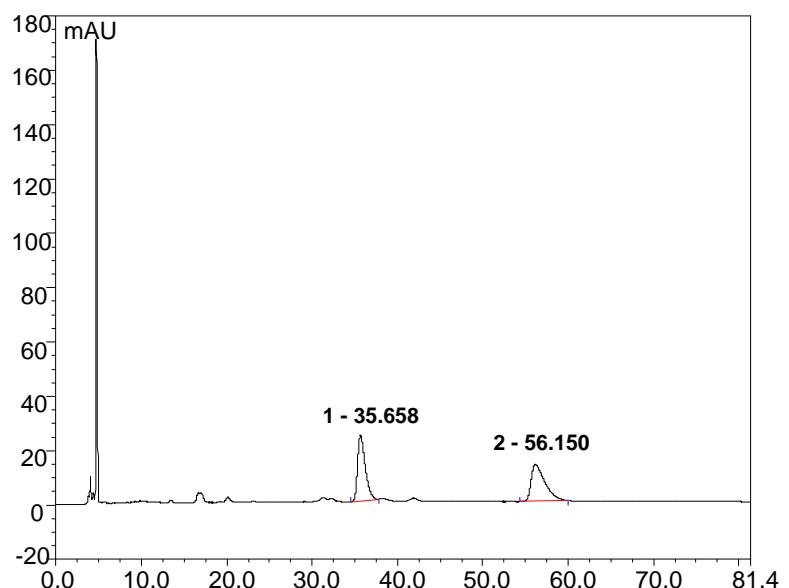
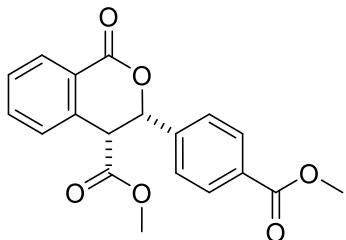
No.	Ret.Time	Rel.Area
	min	%
1	58.78	6.00
2	78.64	94.00
Total:		100.0



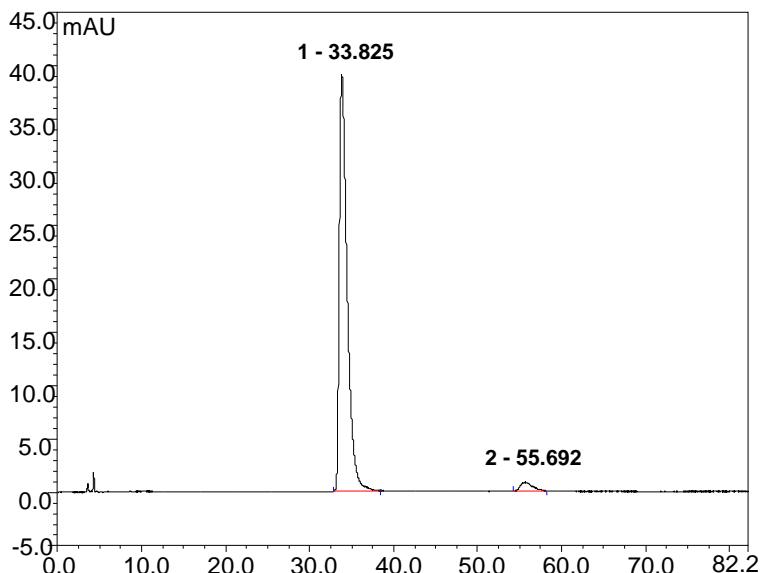
Compound 46 (racemic)

Chiralcel IA (4.6 mm x 25 cm), hexane/IPA: 90/10, 1.0 mL min⁻¹, RT, UV detection at 254 nm.

No.	Ret.Time	Rel.Area
	min	%
1	35.65	49.79
2	56.15	50.21
Total:		100.0



No.	Ret.Time	Rel.Area
	min	%
1	33.82	96.95
2	55.69	3.05
Total:		100.0

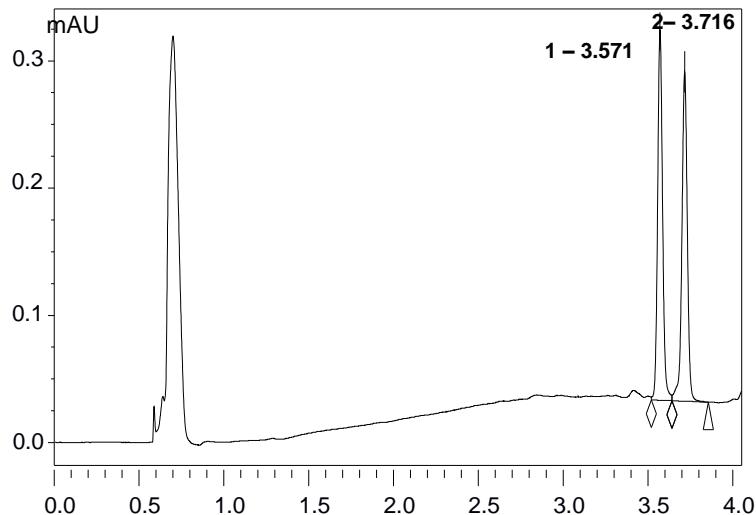
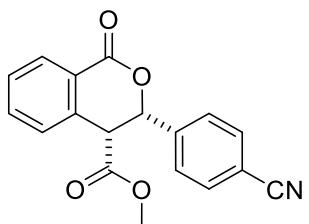


Compound 47 (racemic)

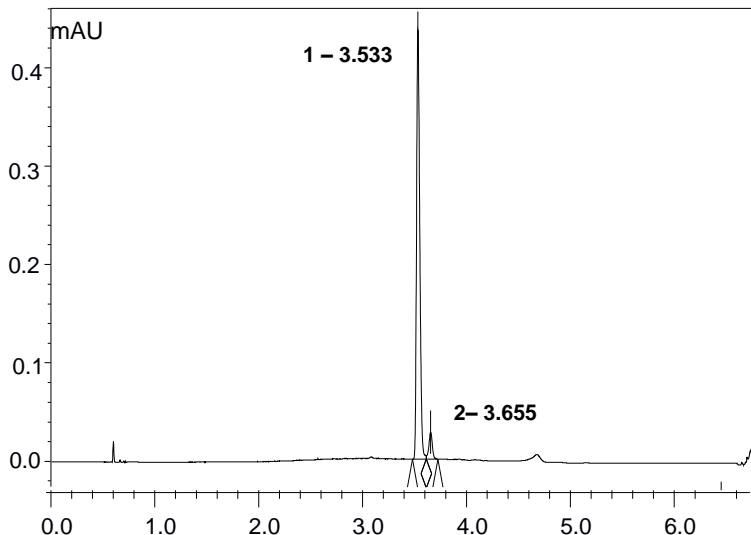
CSP-HPLC analysis. ACQUITY UPC², Trefoil AMY1, 2.5μm (3.0 x 150mm). ABPR: 1500 (psi).

A (CO₂) = 97%/B (Ethanol/IPA 1:1, v:v) = 3%, 1.2 mL min⁻¹, 30 °C, UV detection at 254 nm

No.	Ret.Time	Rel.Area
	min	%
1	3.57	50.69
2	3.71	49.31
Total:		100.0



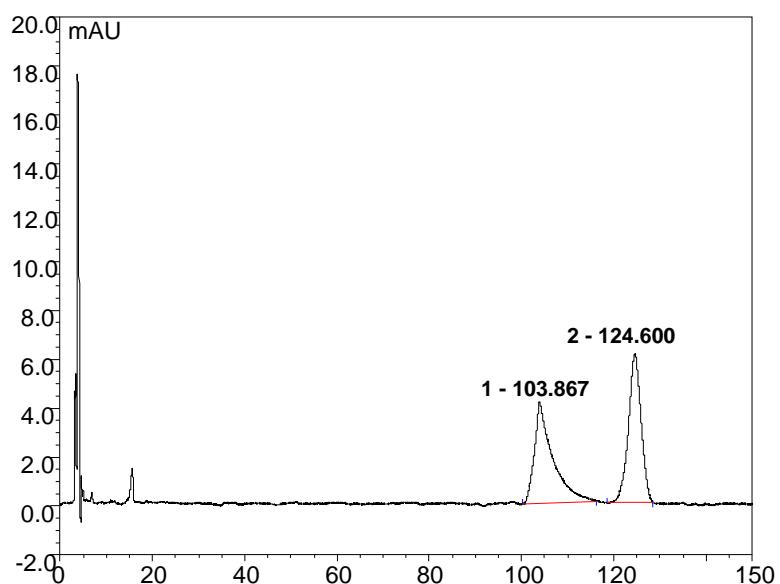
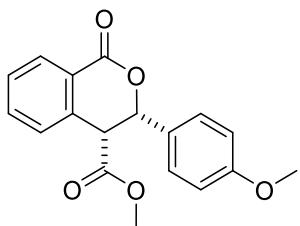
No.	Ret.Time	Rel.Area
	min	%
1	3.53	93.73
2	3.65	6.27
Total:		100.0



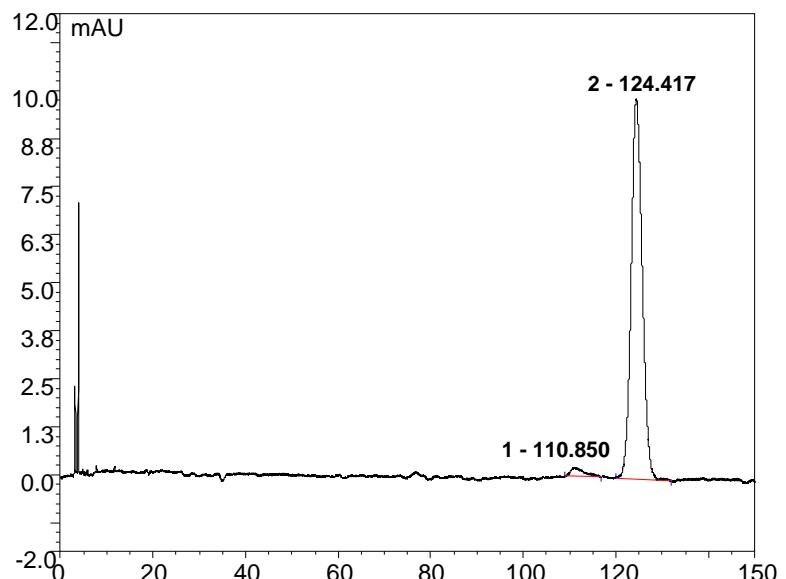
Compound 48 (racemic)

Chiralpak IA (4.6 mm x 25 cm), hexane/IPA: 97/3, 1.0 mL min⁻¹, RT, UV detection at 254 nm.

No.	Ret.Time	Rel.Area
	min	%
1	103.86	49.12
2	124.60	50.88
Total:		100.0



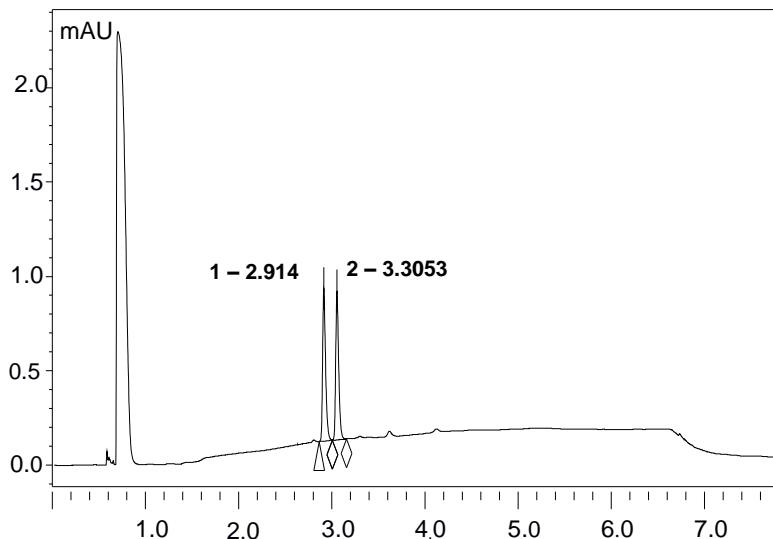
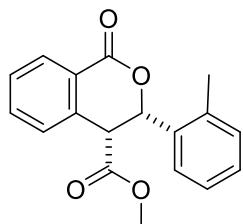
No.	Ret.Time	Rel.Area
	min	%
1	110.85	2.91
2	124.41	97.09
Total:		100.0



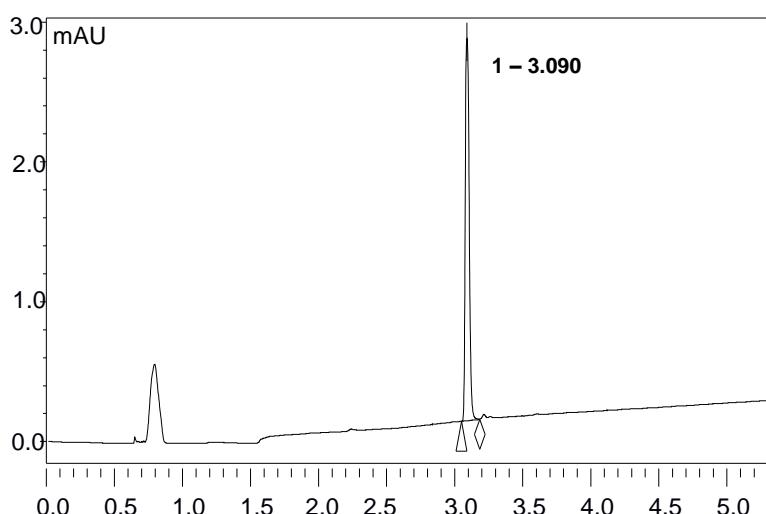
Compound 49 (racemic)

ACQUITY UPC², Trefoil AMY1, 2.5μm (3.0 x 150mm). ABPR: 1500 (psi). A (CO₂) = 99%/B (Ethanol/ACN/IPA 1:1:1, v:v:v) = 1%, 1.2 mL min⁻¹, 30 °C, UV detection at 212 nm

No.	Ret.Time	Rel.Area
	min	%
1	2.91	50.38
2	3.30	49.62
Total:		100.0



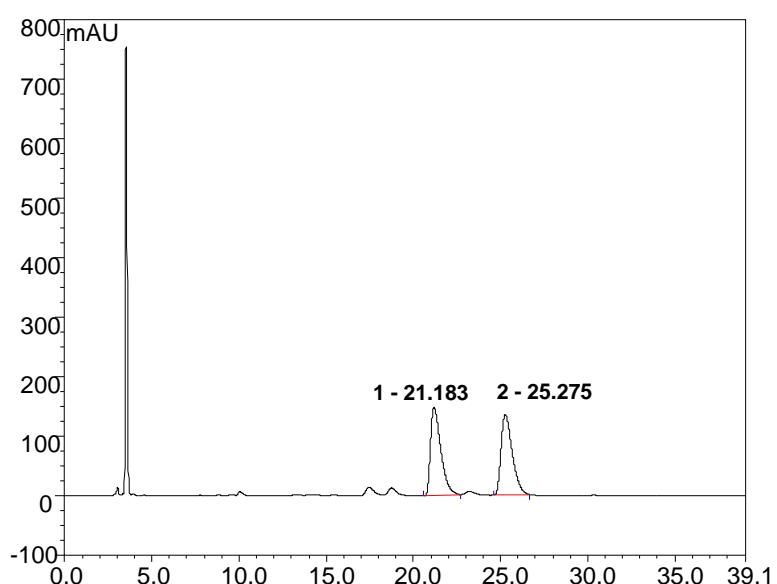
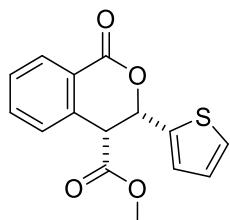
No.	Ret.Time	Rel.Area
	min	%
1	3.09	100
Total:		



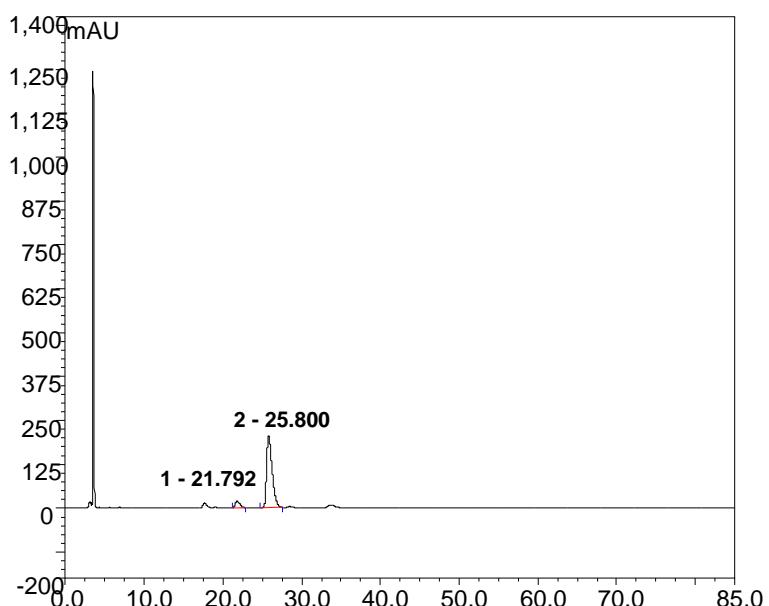
Compound 50 (racemic)

Chiralpak IA (4.6 mm x 25 cm), hexane/IPA: 97/3, 1.0 mL min⁻¹, RT, UV detection at 221 nm.

No.	Ret.Time	Rel.Area
	min	%
1	21.18	49.96
2	25.27	50.04
Total:		100.0



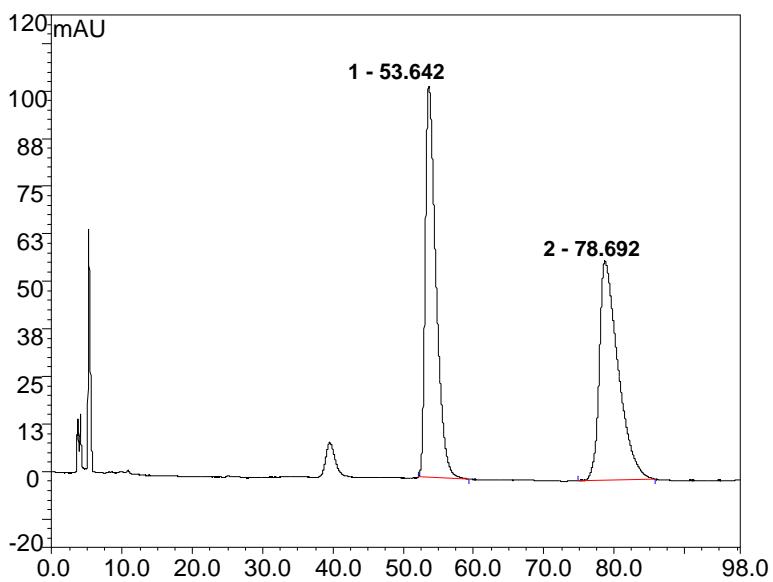
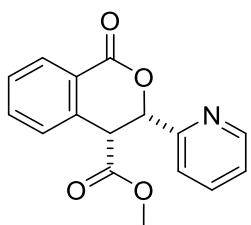
No.	Ret.Time	Rel.Area
	min	%
1	21.79	7.09
2	25.80	92.91
Total:		100.0



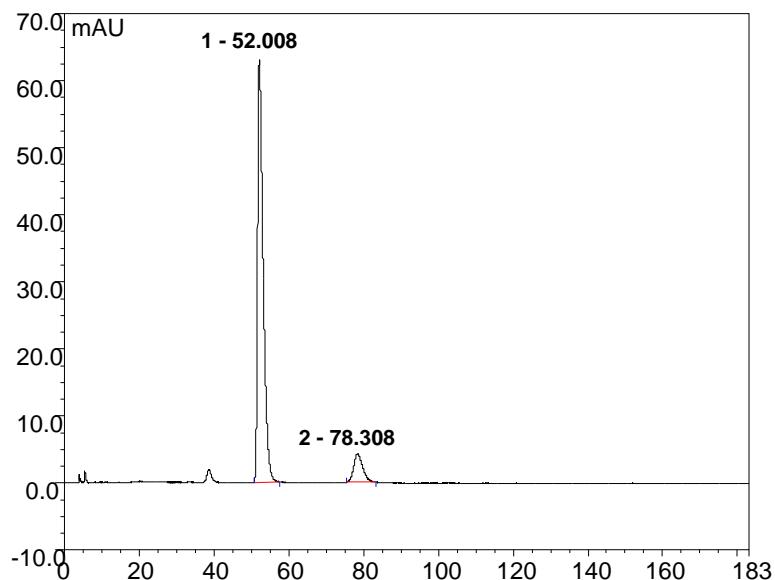
Compound 51 (racemic)

Chiralpak IA (4.6 mm x 25 cm), hexane/IPA: 97/3, 1.0 mL min⁻¹, RT, UV detection at 221 nm

No.	Ret.Time	Rel.Area
	min	%
1	53.64	50.27
2	78.69	40.73
Total:		100.0



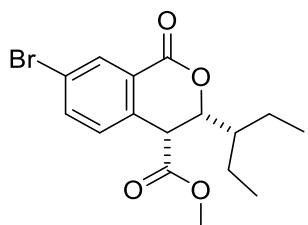
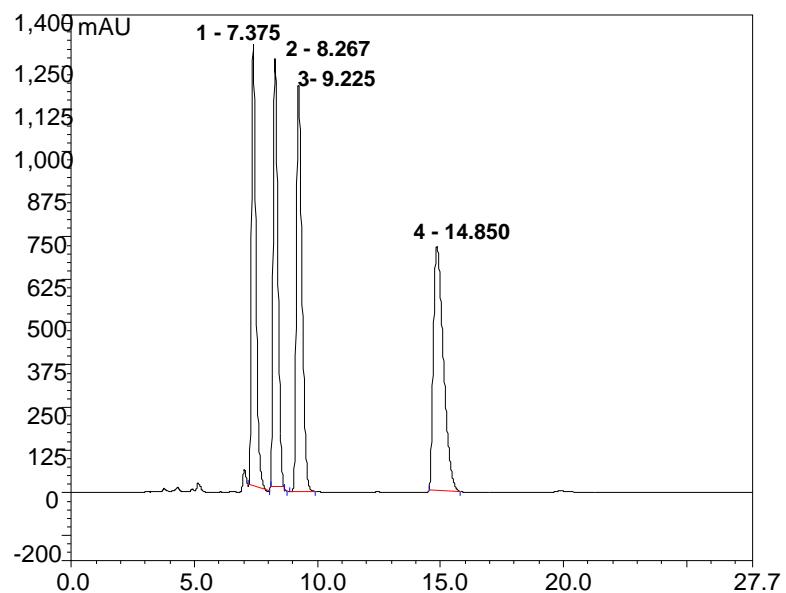
No.	Ret.Time	Rel.Area
	min	%
1	52.01	90.15
2	78.31	9.85
Total:		100.0



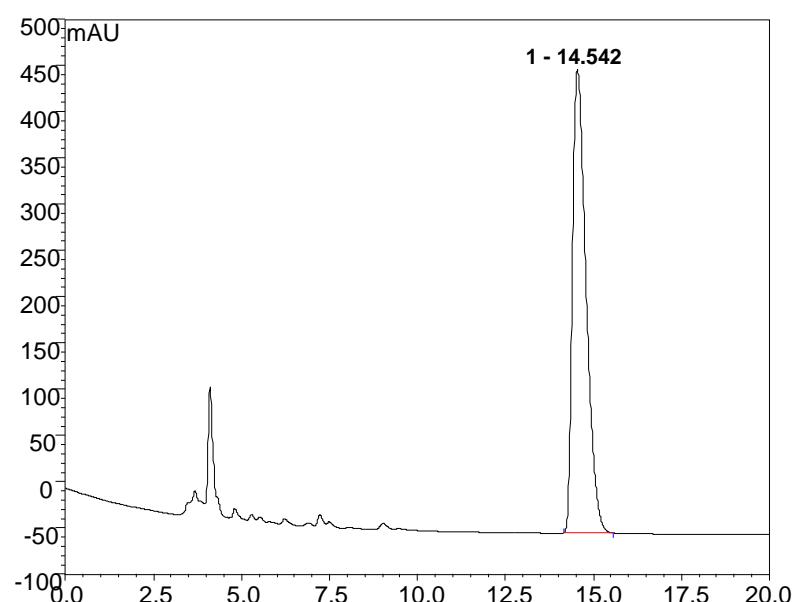
Compound 54 (racemic)

Chiralpak IA (4.6 mm x 25 cm), hexane/IPA: 90/10, 1.0 mL min⁻¹, RT, UV detection at 221 nm

No.	Ret.Time	Rel.Area
	min	%
1	7.37	22.52
2	8.26	23.15
3	9.22	26.18
4	14.85	28.14
Total:		100.0



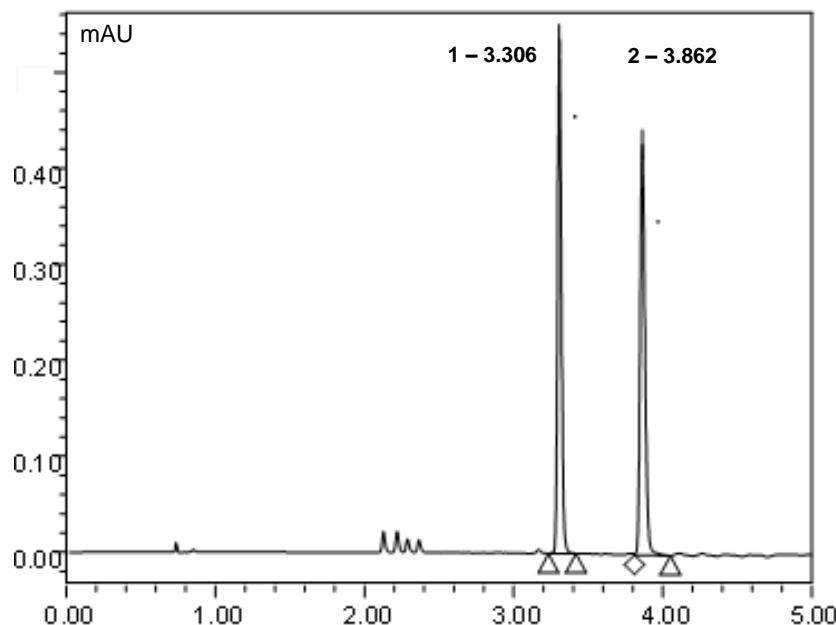
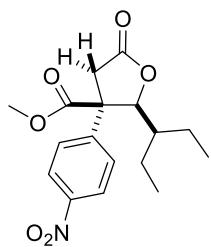
No.	Ret.Time	Rel.Area
	min	%
1	14.54	100.0
Total:		100.0



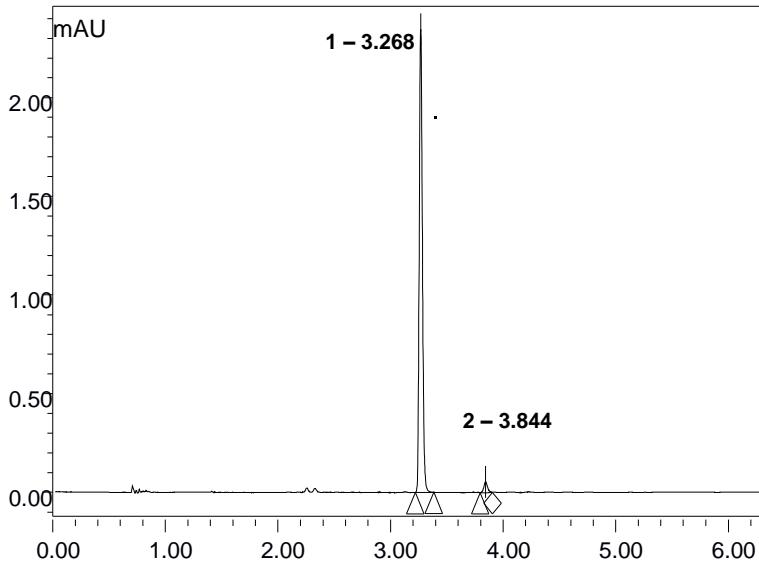
Compound 56 (racemic)

ACQUITY UPC², Trefoil CEL2, 2.5μm (3.0 x 150mm). ABPR: 1500 (psi). A (CO₂) = 97%/B (Ethanol/ACN 1:1, v:v) = 3%, 1.2 mL min¹, 30 °C, UV detection at 254 nm

No.	Ret.Time	Rel.Area
	min	%
1	3.31	49.52
2	3.86	50.48
Total:		100.0



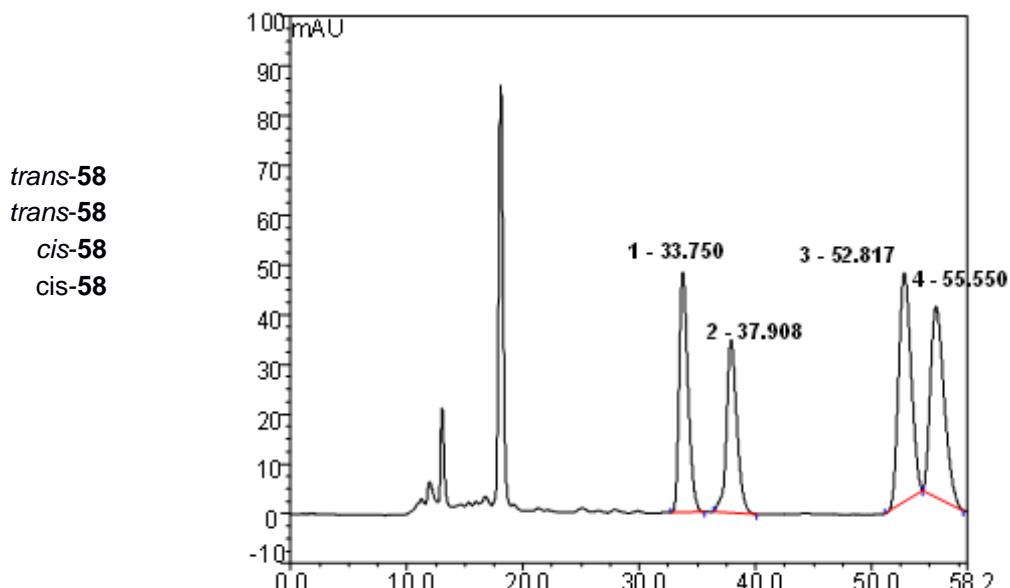
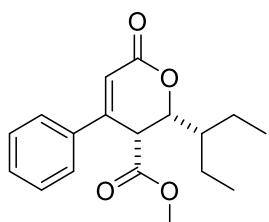
No.	Ret.Time	Rel.Area
	min	%
1	3.26	97.37
2	3.88	2.63
Total:		100.0



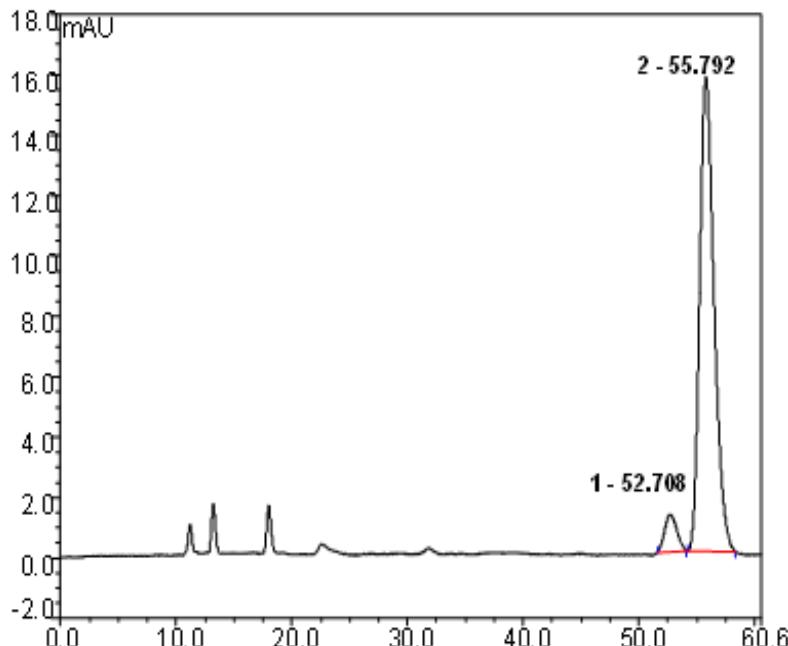
Compound 58 (racemic)

Chiralcel OD (4.6 mm x 25 cm), hexane/IPA: 90/10, 0.3 mL min⁻¹, RT, UV detection at 254 nm

No.	Ret.Time	Rel.Area
	min	%
1	33.75	31.91
2	37.90	14.11
3	52.81	17.57
4	55.55	36.41
Total:		100.0



No.	Ret.Time	Rel.Area
	min	%
1	52.70	6.19
2	55.79	93.81
Total:		100.0

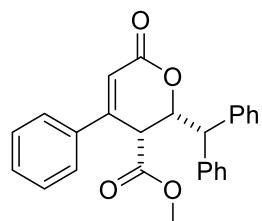
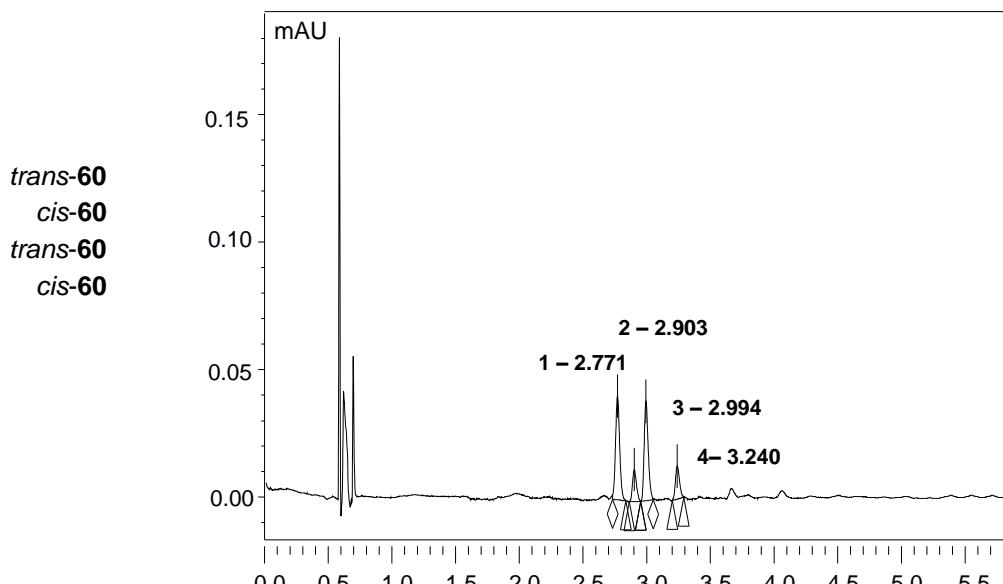


Note: we have had great difficulty in synthesising this racemic product using achiral amines. We solved this by resorting to the use of a 1:1 catalyst mixture of quinine- and quinidine-derived materials to promote the reaction. Since quinine and quinidine are pseudoenantiomeric and not enantiomers, some ee in the ‘racemic’ sample is to be expected.

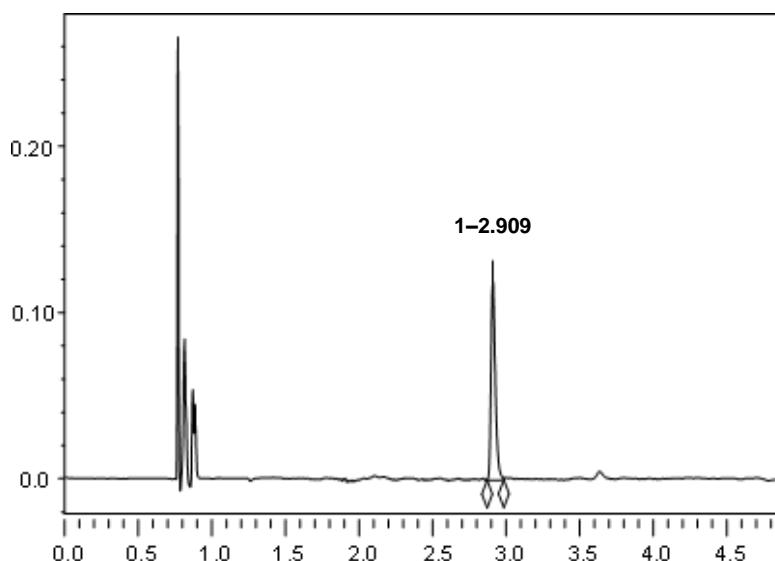
Compound 60 (racemic)

ACQUITY UPC², Trefoil AMY1, 2.5μm (3.0 x 150mm). ABPR: 1500 (psi). A (CO₂) = 97%/B (Ethanol/CAN/IPA 1:1:1, v:v) = 3%, 1.2 mL min⁻¹, 30 °C, UV detection at 254 nm, retention times: 2.9 min.

No.	Ret.Time	Rel.Area
	min	%
1	2.77	39.11
2	2.90	11.59
3	2.99	36.97
4	3.24	12.34
Total:		100.0



No.	Ret.Time	Rel.Area
	min	%
1	2.909	100
Total:		100.0



3 X-ray crystallography of compound 33

X-ray structural analysis for **33** was performed on a Bruker APEXII Kappa Duo at 100(2) K with an Oxford Cobra cryostat, with samples mounted on a MiTeGen microloop using Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). Bruker APEX^[1] software was used to collect and reduce data and determine the space group. Absorption corrections were applied using SADABS.^[2] The structure was solved with the XT structure solution program^[3] using Intrinsic Phasing and refined with the XL refinement package^[4] using Least Squares minimisation in Olex2.^[5] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned to calculated positions using a riding model with appropriately fixed isotropic thermal parameters. The absolute configuration was established by anomalous dispersion effects in diffraction measurements on the crystal. Chirality at C10 and C15 was refined as the *R,R* enantiomer. Crystallographic data, CCDC 1862260, can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

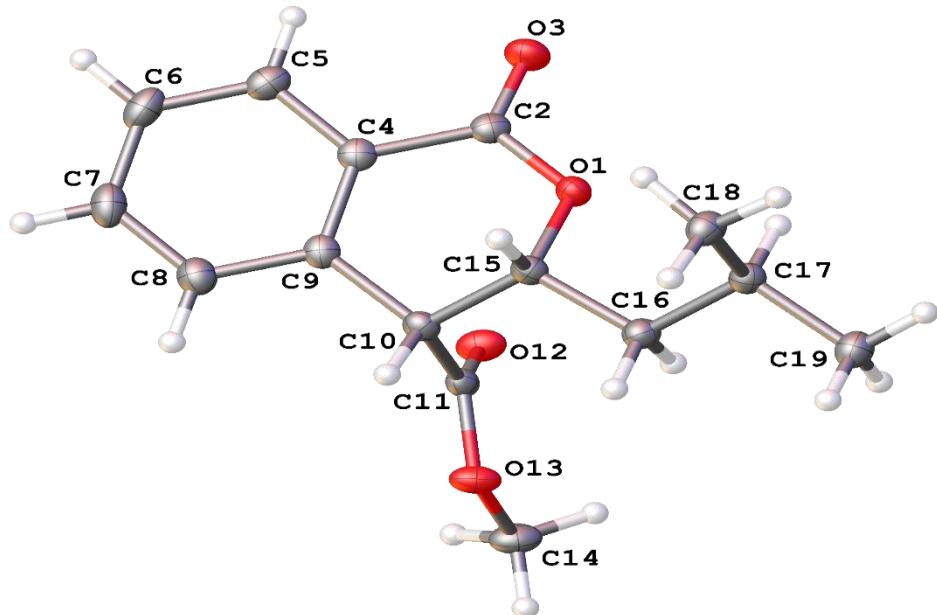


Figure S1 Molecular structure of **33** with atomic displacement shown at 50% probability with chirality at C10 and C15 refined as *R,R* by anomalous dispersion effects.

Table S1 Crystal refinement data of **33**

Empirical formula	C ₁₅ H ₁₈ O ₄
Formula weight	262.29
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	a = 9.1791(4) Å α = 90°.
b = 9.4637(4) Å	β = 90°.
c = 15.3758(7) Å	γ = 90°.
Volume	1335.67(10) Å ³
Z	4
Density (calculated)	1.304 Mg/m ³
Absorption coefficient	0.772 mm ⁻¹
F(000)	560
Crystal size	0.43 x 0.36 x 0.1 mm ³
Theta range for data collection	5.489 to 70.004°.
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -18 ≤ l ≤ 18
Reflections collected	19493
Independent reflections	2503 [R(int) = 0.0393]
Completeness to theta = 67.679°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7533 and 0.6450
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2503 / 0 / 176
Goodness-of-fit on F ²	1.063
Final R indices [I > 2σ(I)]	R1 = 0.0242, wR2 = 0.0657
R indices (all data)	R1 = 0.0243, wR2 = 0.0658
Absolute structure parameter	0.00(3)
Extinction coefficient	0.0085(7)
Largest diff. peak and hole	0.171 and -0.128 e.Å ⁻³

Note: The absolute configuration assignment of the products **31**, **32**, and **34-60** are assigned by analogy to the product **33**

4 Computational study

- **Table S2.** DFT Optimized Geometries (Cartesian Coordinates in Å) of the Stationary Points in PCM-THF.
- **Figure S2.** Pre-TS assemblies leading to (R,S) -**35** and (R,R) -**35** according to binding mode **A**.
- **Figure S3.** Potential energy surfaces for (R,S) -**35** and (R,R) -**35** complexes formed *via* binding mode **A**.
- **Figure S4.** Pre-TS assemblies leading to (R,S) -**35** and (R,R) -**35** according to binding mode **B**.
- **Figure S5.** Potential energy surfaces for (R,S) -**35** and (R,R) -**35** complexes formed *via* binding mode **B**.
- **Figure S6.** QTAIM interactions contributing to the formation of (R,R) -**35** corresponding to binding mode **B**.
- **Figure S7.** QTAIM interactions contributing to the formation of (R,R) -**35** corresponding to binding mode **A**.

Computational Study

The geometry of the isolated molecules as well as those of the different stationary structures of the Potential Energy Surface (PES) were optimized by using the B3LYP^{6,7} density functional theory (DFT) approach, which combines the Becke's three-parameter nonlocal hybrid exchange potential with the nonlocal correlation functional of Lee, Yang and Parr with standard 6-31G(d)^{8,9} basis sets. Vibrational analyses were performed to confirm that the different optimized structures corresponded to true minima of the PES or to transition states. All these calculations were carried out with the Gaussian09 program.¹⁰ The self-consistent reaction field (SCRF) calculations using the PCM solvation model were carried out re-optimizing the gas-phase optimized structures. The dielectric constant in the PCM calculations was set to $\epsilon = 2.379$ to simulate tetrahydrofuran (THF) similar to the solvent medium used in the experimental studies. The temperature for all the calculation was -15°C to mimic the experimental conditions. Finally, more reliable energies for both local minima and transition states were re-evaluated at the B3LYP/6-31+G(d,p) in PCM-THF conditions by a single point calculation.

The characteristics of the intermolecular interactions were analyzed by means of the Atoms in Molecules (QTAIM) theory.¹¹ For this purpose we have located the most relevant bond critical points (BCP), and evaluated the electron density at each of them, by using the QTAIMAll program.¹²

Table S2. DFT Optimized Geometries (Cartesian Coordinates in Å) of the Stationary Points in PCM-THF.

Figure S3 Binding mode A

preTS R, R'

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.66497609 A.U.

B3LYP / 6-31+G(d,p)

SCF Done: E(RB3LYP) = -2990.85627711 A.U.

O 1

C 1.3183117503 2.4555012445 1.5829786666
C 0.8827612205 1.471723342 0.5903601968
C 2.1456934581 0.8345221921 0.5704684369
C 2.6765707565 1.7767097149 1.6032680645
O 3.7142748227 1.9156850438 2.227899605
O 0.7759702974 3.3985930457 2.166618424
N 2.5857137289 -0.2348492554 -0.1050991977
N -0.2861433712 1.2189474123 -0.0207718799
H 1.9300628453 -0.6469223675 -0.7761241136
H -0.2771370532 0.478281769 -0.7430609142
C -1.4054225081 2.1642733656 0.0235672266
C -1.6340753319 2.8173337786 -1.3405660262
C -1.2701381899 4.1797417754 -1.5950399675
C -2.1693433172 2.0811556848 -2.3808492194
C -0.6761257823 5.0438222516 -0.6305967179
C -1.5260517256 4.6846700318 -2.91504107
C -2.3664795757 2.6795710716 -3.6441891116
H -2.4367852127 1.0369241234 -2.2529405036
C -0.3614506855 6.34948187 -0.9616581496

preTS R, S

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.66317108 A.U.

B3LYP / 6-31+G(d,p)

SCF Done: E(RB3LYP) = -2990.85397294 A.U.

O 1

C -0.1485954447 -2.4087759152 -2.0694933611
C -0.0728616711 -1.4140137956 -0.9962903446
C 1.3394267461 -1.3747372266 -1.0395986467
C 1.3723421946 -2.4057089394 -2.1230395998
O 2.2276248869 -2.9733504897 -2.7786769486
O -1.0683051291 -2.9682255201 -2.6691006953
N 2.2347190944 -0.6333410316 -0.3665335724
N -1.0066252048 -0.7542780391 -0.2822944026
H 1.8478754374 -0.0270262857 0.3625464092
H -0.6435870157 -0.1465597948 0.4716168258
C -2.3684865812 -1.2949848523 -0.1538697444
C -2.5588618932 -2.0346670465 1.1737913418
C -2.7070467033 -3.4583131321 1.2386369535
C -2.5628402413 -1.3249599618 2.3603075309
C -2.6869366917 -4.3193571037 0.1038597352
C -2.8825044314 -4.0341310404 2.543149215
C -2.7319184038 -1.9989411933 3.5887648741
H -2.4287700544 -0.247814271 2.3712679865
C -2.8413581421 -5.6852064444 0.2591246258

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 C -0.6299360314 6.8506344218 -2.2658695748
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 H -0.3704281746 7.8818416163 -2.4843254
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 N -2.0709418213 3.936374879 -3.9154223734
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 H 0.9391373577 7.7069422177 1.7067167434
 H 1.1577513951 5.9875844094 1.2642555508
 H -0.4531782843 6.5862461142 1.7459783367
 C -2.1602078752 1.7187485204 2.9943916657
 C -3.3658833937 2.6737910669 3.1570189343
 H -1.9984131619 1.0913206685 3.8727938858
 C -2.6926540742 1.4721127404 0.5261469621
 C -3.6520061064 -0.0856923912 2.1883437408
 C -4.4610998637 2.2898494154 2.1439634823
 H -3.0497926532 3.7079781942 2.9882716201
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 H -5.1820697531 0.7643813956 3.473839258
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 N -2.4441147847 0.765669291 1.8545573793
 C -6.0686087776 0.3704795031 1.587308959
 C -7.2871359979 0.1392936156 2.0779507906
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 H -8.1079271073 -0.1743799526 1.4388212779
 H -7.5108691992 0.2542716766 3.1369979069
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 H -3.1534019157 -7.3259097818 1.629489048
 O -2.8235485223 -6.5891613999 -0.75528361
 N -2.8964760227 -3.3039625725 3.6936128294
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 H -2.6676963865 -6.9924163601 -2.7265028464
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 O -3.3984018638 2.9419214079 1.5689066829
 H -2.7066092616 -0.9896668823 -2.8646242736
 H 1.5912096101 2.8687643684 2.8741833424
 H 0.5787529729 2.035962461 -0.9995684264
 H -2.211955675 0.9758645843 -1.5935271369
 H -2.7362888574 -1.4281993184 4.5161385952

C 3.9966495281 -0.7019608761 -0.1470290083
 C 4.3971105316 -1.3849403355 1.1863314415
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 C 3.5316383527 -1.4626398891 2.2832020116
 C 6.0388608105 -2.6650911544 2.4564029322
 H 6.3290130035 -1.9986130847 0.4400552841
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 H 2.5399840977 -1.0292062478 2.233771467
 C 5.1731550012 -2.7203672523 3.5515625654
 H 7.0163675765 -3.1372256544 2.50667921
 H 3.229494931 -2.1599231776 4.2953752069
 H 5.4718459901 -3.230278174 4.463324897
 C 4.8871598643 0.5102665936 -0.5234848246
 C 4.5548562346 1.2357071895 -1.6808171007
 C 5.9869653246 0.9330757333 0.228356591
 C 5.3094235937 2.3355499001 -2.0830156978
 H 3.6952327195 0.9339192981 -2.2724542481
 C 6.7483959463 2.0346675785 -0.1749684056
 H 6.2491656508 0.4205002378 1.1452083185
 C 6.4169939575 2.7383395791 -1.331199363
 H 5.0313946226 2.8778774036 -2.9827805407
 H 7.5969936074 2.3447395271 0.4289921903
 H 7.0080438076 3.5957551253 -1.641611411
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 C 5.086203657 -1.8660716594 -2.1863118788
 C 3.111695168 -2.8427584744 -1.2160762241
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 H 5.8402200669 -1.0881407494 -2.2197758563
 C 3.1711196768 -3.8876143093 -2.1370933386
 H 2.3210924011 -2.8403884798 -0.4723094037
 C 4.19376913 -3.9305325046 -3.0880831907
 H 5.9571693072 -2.9391426166 -3.8340277102
 H 2.4192902797 -4.6712051132 -2.1052952442
 H 4.2432526465 -4.7461543125 -3.8041679946
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 C -0.2549548688 -4.9612540153 2.2176768557
 C -0.5366897194 -3.628671603 4.4182909287
 H 0.996918279 -3.3204874292 2.920389733
 H -1.3298291169 -5.187369215 2.1679648391
 H 0.1953425635 -5.7533388095 2.8246770008
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 H -1.5962241123 -3.9162243037 4.4567994691
 C 0.2857289291 -4.5577160119 5.3185732574
 H -0.0489539797 -4.4663786347 6.3576996456
 H 0.1840596762 -5.6086770004 5.0309326182
 H 1.3503954128 -4.2985882345 5.2838928176
 C 0.3530910955 -5.0003394377 0.8112248314
 H 1.4347897086 -4.824740993 0.848222205
 H 0.189083404 -5.9771049529 0.3433454535
 H -0.0848206325 -4.2432561359 0.1487888371

min02_cis-RR

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.65210811 A.U.
 B3LYP / 6-31+G(d,p)
 SCF Done: E(RB3LYP) = -2990.84027114 A.U.

0 1

C 3.6897729118 -0.943052576 -0.2544176176
 C 4.449110029 -0.5928497984 -1.557475832
 C 3.8044029763 -0.1220405716 -2.7054077452
 C 5.8512357051 -0.6837715234 -1.5773731255
 C 4.533424719 0.2290613932 -3.8464298667
 H 2.7270848082 -0.0154967065 -2.7204521879
 C 6.5797713239 -0.3413346857 -2.7151121738
 H 6.3814819683 -1.0167126444 -0.690071712
 C 5.922432968 0.1171045532 -3.859779436
 H 4.005481691 0.5895814812 -4.72528422
 H 7.6631522497 -0.4252632312 -2.7027724801
 H 6.4881956792 0.3887153172 -4.7466800567
 C 3.8236292684 -2.4289678914 0.1666270282
 C 3.1300396599 -2.8542844044 1.3136248412
 C 4.5656707774 -3.375664096 -0.545673206
 C 3.192941807 -4.1774417098 1.7443485592
 H 2.5335547058 -2.1399474271 1.8742374241
 C 4.631839563 -4.7046696457 -0.1141525693
 H 5.0835572865 -3.0912526558 -1.4529209462
 C 3.9509235946 -5.1111264245 1.0315366533
 H 2.6486504253 -4.4789566101 2.6352382572
 H 5.2129896789 -5.4218525904 -0.6876271702
 H 4.001691661 -6.1444602944 1.363794954
 C 4.2435082958 0.015758123 0.8344403533
 C 5.0833432305 -0.4176265413 1.8667454289
 C 3.9572727161 1.3872543501 0.7400499289
 C 5.6091932035 0.4916814071 2.7898395722
 H 5.3320882456 -1.4684948716 1.9597452328
 C 4.4744465053 2.2936231765 1.6639641642
 H 3.337203734 1.7543356052 -0.0723125478
 C 5.3032831863 1.848383816 2.6973891605
 H 6.2577259754 0.1302535308 3.5832624227
 H 4.235700123 3.3495583491 1.5699988908
 H 5.7097807171 2.5536837908 3.4169180428
 C 0.8077959625 3.8593253953 -2.2733106414
 C 1.7570114893 3.3805207635 -3.4086132949
 C 1.5346863251 4.582995441 -1.1067647266
 H 0.0529120149 4.5210844299 -2.7176191129
 H 1.1570802228 2.8429615733 -4.1540115008
 H 2.4715085842 2.6544966979 -2.9975938218
 H 1.1207156541 4.2473136906 -0.1463219204
 H 2.5915720533 4.285209209 -1.0945105743
 C 2.5236015494 4.5122958678 -4.1006108784
 H 3.1953918732 5.0318714358 -3.4097489614
 H 3.1358028068 4.1087289042 -4.9146551822
 H 1.8384675894 5.2526186527 -4.5296309112
 C 1.4222975017 6.1112010797 -1.1705389587
 H 1.9508887867 6.5727155913 -0.3291208132
 H 1.8466399351 6.5143482247 -2.0958301247
 H 0.3737405754 6.4273421565 -1.1196207498

min02_trans-RS

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.65567263 A.U.
 B3LYP / 6-31+G(d,p)
 SCF Done: E(RB3LYP) = -2990.84532380 A.U.

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 O 3.3238243661 1.5472218955 2.5375053557
 O 0.2633472873 2.7422711528 2.5824884487
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 C -0.765764748 3.9609247684 -1.2845018024
 C -1.5936755259 2.0431103641 -2.4904169652
 C -0.4356491995 4.701223209 -0.1128206408
 C -0.537981248 4.5629963776 -2.5691976251
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 H -2.0190828638 1.0452051324 -2.5488913159
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 H -0.5653329125 4.2559120895 0.8636316107
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 C 0.3146399838 6.5683695897 -1.486968083
 H 0.1698841756 6.3091970591 -3.6102573295
 H 0.7307285062 7.5704477244 -1.5233793451
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 H 0.7724593161 5.3195644956 2.3337593679
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 C -4.7945982941 0.1537238104 1.1965866456
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 H -4.3605814591 2.6062914161 3.5952553082
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 H -4.6571908102 2.6821733169 -0.720181564
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 H -1.3958887287 2.5081718243 0.8805543698
 N -3.3487762108 0.4973590919 1.2475700122
 C -6.8943625859 1.4432641175 0.5610846626
 C -8.1753054619 1.4109728665 0.9357303971
 H -6.6597872588 1.5105428716 -0.5028696567
 H -8.9849402669 1.4586482535 0.2119461946
 H -8.4633310467 1.3356781432 1.9829697873
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 O -3.2900875282 -2.3520505369 0.824636737
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 C -3.129221667 -5.6805674886 -1.3100309581
 C -0.8712741138 -2.0472664201 -1.9887993174
 C -0.5034094104 -1.2853900968 -0.7842316112
 C 0.8144957402 -1.7961541378 -0.7916707007
 C 0.5406128114 -2.6110986507 -2.0115257709
 O 1.1694930017 -3.3685266592 -2.7289713287
 O -1.8837857446 -2.1517652206 -2.6773216879
 N 1.8773403501 -1.5694983047 0.0011725443
 N -1.17698267 -0.4122575486 -0.0111121992
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 C -3.229604691 -1.0903959166 1.1589855367
 C -3.9166055031 -2.3418500357 1.036262814
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 H -3.7469904655 -2.5984447637 -1.1194715689
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 N -4.2240680671 -2.3967848121 3.4838837846
 C -4.6533946865 -4.4031808179 -2.6125275686
 H -4.9462687208 -5.14197383 -3.3597230586
 H -3.5687934617 -4.253798488 -2.6417019592
 H -5.1523493469 -3.4493745336 -2.8237456314
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 C -4.3528042291 1.2186502536 -2.7789264852
 H -2.3852850383 2.0997995652 -3.2369995736
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 C -5.1158145479 1.8485967613 -1.597327903
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C -2.7427838586 -4.3379797959 -1.2973436028
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 C -4.8099125008 -5.2011923119 -2.9962988448
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 C -1.7078354728 -3.8195716376 -0.3337114473
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 C 3.8969828867 -0.7207212592 -0.1355884324
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 H 6.3262544934 -1.9659394132 -0.0560203502
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 H 2.8488756292 -1.3321884878 2.3928947242
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 C 0.3691713177 4.6877866876 2.0502412721
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 O -0.4437731849 2.3882623599 2.2137523949
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 H -0.8636614833 2.5550594075 -0.8313044248
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 H 7.3425462051 -2.7803457346 -1.8718233791
 H 6.7010915372 -1.4344135009 -3.8712214612
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 H 1.3880192991 -7.605831271 0.4205303892
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 H 5.5963591999 -0.7700730204 4.6588647094
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 H 0.3899146475 3.9476363457 -2.8027173636

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 H -0.6621422472 -1.3885113885 4.2642809804
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Prod cis-*RR*

B3LYP / 6-31G(d)
 SCF Done: E(RB3LYP) = -2990.67713012 A.U.
 B3LYP / 6-31+G(d,p)
 SCF Done: E(RB3LYP) = -2990.86735141 A.U.

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 C 2.603185603 1.967550217 1.5536163108
 O 3.682660669 2.2697978181 2.030893344
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 H 1.7771224137 -1.0745040621 0.0732136338
 H -0.5696837446 0.205974189 -0.2834744296
 C -1.5010309875 2.0994480984 0.0990851533
 C -1.6249849755 2.5577338859 -1.3573498074
 C -1.2845938468 3.8899577868 -1.7620134289
 C -2.0695918604 1.6751638014 -2.3246033194
 C -0.7689784097 4.888693157 -0.8861790702
 C -1.4753580355 4.2167198881 -3.1479446051
 C -2.2065321349 2.1056478942 -3.6620115691
 H -2.2931369655 0.6416628036 -2.0809308829
 C -0.4657604938 6.1506306093 -1.3641413759
 H -0.5625305358 4.6505942525 0.1485399128
 C -1.1639138025 5.5317760473 -3.5951079773
 C -0.6752340088 6.4765945371 -2.7329344511
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 H -0.429636607 7.4798231614 -3.0672048371
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 H -2.3059066395 1.6119552566 4.0076482272
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 C -3.9476101885 0.293612628 2.4426064349
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 H -3.0994090636 4.1316651919 2.6495995139
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H 1.1354668934 2.4271695308 -3.2707726721
 H 3.6021648069 2.0509480072 -0.7647106351
 H 3.4104220706 1.9516899184 -2.491509029
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 H 3.0546066322 3.6591454259 -4.322563773
 H 1.515951869 4.2417297421 -4.9612556232
 H 2.3892395652 5.2013160814 -3.7580823304
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 H 5.5781490232 3.0023927418 -1.8951311253
 H 4.5815648668 4.214437252 -2.7129375559
 H 4.760624876 4.2605278509 -0.9582422639

Prod trans-*RS*

B3LYP / 6-31G(d)
 SCF Done: E(RB3LYP) = -2990.68283080 A.U.
 B3LYP / 6-31+G(d,p)
 SCF Done: E(RB3LYP) = -2990.87373046 A.U.

0 1

C -1.2218934208 -2.2865618716 -1.7244671731
 C -0.7614415619 -1.4571107085 -0.6073482438
 C 0.5745556197 -1.9038734548 -0.7364746463
 C 0.2034999284 -2.7856807164 -1.8894401254
 O 0.7884842364 -3.5234927568 -2.6625866379
 O -2.3014109349 -2.4492967036 -2.2963719033
 N 1.6798371682 -1.5848575464 -0.0491381016
 N -1.3904948248 -0.5736386531 0.1929779227
 H 1.5870206049 -0.7836501167 0.5774950238
 H -0.8075659582 -0.0561180391 0.8646414929
 C -2.8507349779 -0.6291261337 0.3394898465
 C -3.262362724 -1.4120820024 1.5934556147
 C -3.9602633623 -2.6605989952 1.5305855882
 C -2.931799756 -0.9149899315 2.8406976331
 C -4.325690323 -3.3139546982 0.3186123316
 C -4.2980830063 -3.2798313425 2.7828107012
 C -3.3020725084 -1.6163720215 4.0072347867
 H -2.379394506 0.0146892552 2.9466453558
 C -5.0021278742 -4.5199970777 0.351150187
 H -4.0302636898 -2.8953945083 -0.6338304962
 C -5.0067720333 -4.5143940555 2.7705382505
 C -5.3539997423 -5.1197109742 1.5926930657
 H -5.2559771792 -4.9604373555 3.7282241939
 H -5.8891175478 -6.0640463029 1.5746169435
 O -5.377566711 -5.2292344984 -0.7448459777
 N -3.9722635728 -2.7533400044 3.9962732183
 C -5.0768235853 -4.6932263833 -2.0343889907
 H -5.4349217076 -5.4324014704 -2.7520708397
 H -4.0007080932 -4.5367524439 -2.1646458759
 H -5.5999369753 -3.742371685 -2.1946914189
 C -3.0330179765 1.2600828687 -2.0444694979
 C -4.531060336 1.0042458154 -2.3385001328
 H -2.5990666171 2.0512213492 -2.6594466174
 C -3.5160770426 0.7697175223 0.3789723429
 C -3.5524791369 3.0876164589 -0.4666723251
 C -5.3776687264 1.5266398844 -1.1593303348
 H -4.7087580194 -0.066280921 -2.4846720684
 H -4.8187551408 1.5090911861 -3.2655485916
 H -3.3063227511 1.2376084231 1.3418942434

C -4.0141460169 2.5805246783 0.6189074024
 C -5.1204890265 1.3106627584 2.5469954277
 H -4.1277726031 -0.4678857821 1.6813602603
 H -3.7337982767 -0.19606001 3.394481979
 H -5.4341185108 3.4016797249 2.0373591758
 H -4.7762978864 2.2778768199 -0.1033890777
 H -3.6509799473 3.564532488 0.3044003252
 H -5.3806576743 1.4397354895 3.6036960913
 H -1.2193018549 2.9493344832 0.7163417597
 N -2.6871689973 1.0279953667 2.0330119567
 C -6.3462052808 0.8123914893 1.8220638053
 C -7.5621618252 0.7602692488 2.3679923104
 H -6.1998653 0.4713720577 0.798041697
 H -8.4227911411 0.4068209469 1.8066642996
 H -7.7445860881 1.0686196017 3.3959571888
 C -2.4808937182 -3.8245992049 0.298048223
 O -3.3846142538 -2.6786665539 0.4139973894
 C -2.8581964792 -3.8511960347 -4.4563333721
 C -2.008623758 -3.9834550186 -3.3551630108
 C -2.3766974376 -3.4584669963 -2.1153159362
 C -3.6095058936 -2.7921810155 -1.9994270176
 C -4.4544124586 -2.6447486474 -3.10506258
 C -4.0818128241 -3.1838366345 -4.3342436426
 H -2.5645871576 -4.2713176457 -5.4144827018
 H -1.0561320314 -4.49656625 -3.4599351826
 C -1.5191887737 -3.5467167964 -0.8781902272
 C -3.9768728165 -2.185167376 -0.6969835551
 H -5.3931090807 -2.1125874067 -2.9871369985
 H -4.7370120042 -3.0831186375 -5.1945028766
 C -0.7050474717 -2.2321175194 -0.6314221983
 O 0.3783180449 -2.3430461857 -0.0059541481
 O -1.2240187445 -1.1588165859 -1.0528204725
 O -4.7753550257 -1.2683018291 -0.5686434333
 H -1.3903311618 2.5274699625 2.8039633656
 H -1.8981437958 0.3714000705 1.9997179412
 H -3.1052344981 -4.6903646647 0.0358594187
 H -0.8057756003 -4.3692099502 -0.9632464437
 H -2.5615160608 1.4030609165 -4.4145905848
 C 3.9261017264 -0.7354493729 0.225817843
 C 4.5319392429 -1.1603722341 1.589029765
 C 5.7903331298 -1.7863077789 1.6201078018
 C 3.8570354778 -0.9836193315 2.8007521046
 C 6.3641688999 -2.1937627236 2.8231644086
 H 6.3238671608 -1.9659657914 0.691366705
 C 4.4257163057 -1.4000652457 4.008701322
 H 2.8725946809 -0.5327633784 2.8154936466
 C 5.6828494986 -2.0010452029 4.0278815464
 H 7.3402671675 -2.6715631937 2.8167183363
 H 3.8765984863 -1.2523529733 4.9349154254
 H 6.1246762653 -2.3238476665 4.9666317565
 C 4.6583496118 0.4705490966 -0.4182588346
 C 4.075764343 1.0870814798 -1.539147102
 C 5.882611343 0.9650204185 0.0424143299
 C 4.7000985041 2.1557594592 -2.1806806327
 H 3.1246073995 0.7223717399 -1.9148072076
 C 6.512533523 2.0344528336 -0.6005751122
 H 6.3472893903 0.5337607106 0.9201490234
 C 5.926655315 2.6347681772 -1.7139020239
 C -5.0438724519 0.7058272772 0.1040505753
 C -5.0278973483 3.0254698009 -0.9459155703
 H -3.4642168621 3.3497759542 0.5897653711
 H -2.9488263359 3.7888659754 -1.0446819173
 H -6.4419505399 1.4278514027 -1.3907148824
 H -5.5989377082 1.0775082002 0.9693886406
 H -5.3560861016 -0.3329331888 -0.0442219877
 H -5.1012129163 3.5196526754 -1.9216016959
 H -3.2108814503 -1.1466860604 -0.5479064048
 N -2.903003036 1.7291582174 -0.6196636567
 C -5.9503595992 3.7438011761 0.0051228704
 C -6.7406112571 4.7617466721 -0.338844049
 H -5.9545884752 3.3937215627 1.0383153664
 H -7.3957394619 5.2431627734 0.3820372648
 H -6.7621349192 5.1525143106 -1.354287523
 C 1.8823284078 2.7728734937 -1.1018832211
 O 0.6851387515 3.0773741502 -1.8892787092
 C 1.017925635 6.6041078599 1.706294482
 C 1.4746094622 5.2860423082 1.6285929403
 C 1.1447260101 4.4895814771 0.5303378827
 C 0.3409456254 5.033335365 -0.4857978165
 C -0.1268110505 6.349638531 -0.4039492004
 C 0.2188803349 7.1390349308 0.6905878244
 H 1.2866931657 7.2161035587 2.5629244877
 H 2.0868366135 4.8744890985 2.4269653433
 C 1.5693794839 3.0528495816 0.3836238921
 C -0.0551179282 4.1788977782 -1.6324249019
 H -0.7538329002 6.7381049509 -1.2001245913
 H -0.1339060808 8.1640668393 0.75597772799
 C 0.4544118193 2.0524314327 0.827678029
 O 0.8272123175 0.9013887351 1.1810953203
 O -0.7410201242 2.4507556675 0.7538657272
 O -1.0178213639 4.4060559987 -2.3506013437
 H -2.4259091946 0.3634972349 -2.1625884839
 H 2.4586352706 2.8404261985 0.9815875152
 H 2.0014831682 1.6946681039 -1.2447806837
 H -1.9052253441 1.8579361185 -0.3207226534
 H -3.0378153695 -1.2118240514 4.9830865694
 C 3.0017539957 -2.2714434386 -0.0864142541
 C 3.8721415054 -1.7423921587 -1.2572190121
 C 3.3002854719 -1.2146810302 -2.4213558053
 C 5.2723254703 -1.8222256789 -1.1874643143
 C 4.1001039341 -0.782876073 -3.4832217036
 H 2.2250483383 -1.1370230453 -2.5165355096
 C 6.0729873449 -1.3932457998 -2.2467852251
 H 5.7453408132 -2.2223879169 -0.2966075764
 C 5.4901161093 -0.8689582002 -3.401944601
 H 3.6283432558 -0.3823455522 -4.3764323656
 H 7.1541145091 -1.4664231252 -2.1639820207
 H 6.1112387599 -0.5325968124 -4.2274989109
 C 2.7630199142 -3.7967512564 -0.1805227775
 C 1.8239939802 -4.3912704393 0.678700962
 C 3.4780229099 -4.6204156682 -1.0550077824
 C 1.6023904747 -5.7670747975 0.6571848224
 H 1.2671505355 -3.7717650711 1.3753706863
 C 3.2612475804 -6.0011837957 -1.0742333799
 H 4.2036370637 -4.1908182992 -1.7355178114
 C 2.3221552226 -6.5803096302 -0.2222382193

H 4.2262371781 2.6132738993 -3.0450782529
 H 7.4608132554 2.4019067642 -0.2173772266
 H 6.4151461523 3.4689558293 -2.210235744
 C 3.9870636076 -1.982888635 -0.7031444157
 C 4.7026283972 -2.007850448 -1.9059870183
 C 3.3459203594 -3.1609813428 -0.2877915579
 C 4.7629887801 -3.1719355714 -2.6795435768
 H 5.2246563346 -1.1230485811 -2.2493713897
 C 3.3977667109 -4.3184746773 -1.0612788173
 H 2.8026289569 -3.1752348209 0.6503712187
 C 4.1087737197 -4.3300680214 -2.2641766349
 H 5.3276683065 -3.1653026003 -3.6080957871
 H 2.8872326822 -5.2144232387 -0.7182433583
 H 4.155690002 -5.2339678516 -2.865617005
 C -1.8496731229 -4.0783095877 1.6767756472
 C -1.0264093456 -5.4015761975 1.6427911376
 C -2.9232664614 -4.1073242698 2.7867497929
 H -1.1639355229 -3.246477348 1.8810151151
 H -1.0282881889 -5.8248143574 0.6304816364
 H -1.5262701121 -6.1519464503 2.2684048802
 H -3.5384653022 -3.2043667791 2.720744605
 H -3.6003606115 -4.9549748835 2.6046549403
 C -2.3449656964 -4.2106799778 4.202971367
 H -3.1473568419 -4.2045216674 4.9496164056
 H -1.7687235293 -5.1310461506 4.3485697847
 H -1.6798825176 -3.3657482874 4.4214529385
 C 0.4275682888 -5.2345345568 2.0978696031
 H 0.4830889389 -4.8725813475 3.1313500515
 H 0.9707671787 -6.1856319146 2.0471715502
 H 0.9368292054 -4.5053386103 1.4600564721

TS C-C *R,R*

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.63734491 A.U.

B3LYP / 6-31+G(d,p)

SCF Done: E(RB3LYP) = -2990.82545320 A.U.

0 1

C -0.8723028482 1.8657535042 -1.9303014261
 C -0.5498009715 0.9586901432 -0.8244997513
 C -1.8362788842 0.3760632767 -0.8358484035
 C -2.2715963513 1.2698536332 -1.9574448606
 O -3.2811922033 1.4295014843 -2.6166836806
 O -0.2502227479 2.7212438132 -2.5597967939
 N -2.394266095 -0.5994536964 -0.1065883989
 N 0.5869893941 0.7788403226 -0.1092783113
 H -1.7776805903 -1.0885095875 0.5369153827
 H 0.5461753108 0.0962785426 0.6457415885
 C 1.5061094043 1.9216097024 0.0648908817
 C 1.199438537 2.6748233252 1.3658183673
 C 0.5852713695 3.9696934895 1.3757044588
 C 1.4801650963 2.0791840584 2.582361157
 C 0.2354383998 4.7011719623 0.2044293755
 C 0.3168018339 4.5524165861 2.6614886244
 C 1.1670322931 2.7451281258 3.7868161775
 H 1.9412068183 1.0976111391 2.6376894853
 C -0.3522362023 5.9493699643 0.306642466
 H 0.3938477991 4.269044431 -0.7739682973

H 0.8685998317 -6.2032417586 1.3297210646
 H 3.8260977831 -6.6201250796 -1.7662053362
 H 2.1504532659 -7.653100821 -0.2416532956
 C 3.7080108423 -1.9152187837 1.2529420411
 C 4.31966811 -2.8851233486 2.0569621248
 C 3.800684516 -0.5716570944 1.6516427878
 C 4.9903419423 -2.5264167955 3.2304236014
 H 4.2804141323 -3.9298549473 1.7724091403
 C 4.4575455853 -0.2141825954 2.8282794092
 H 3.3483927565 0.2105201373 1.0511928886
 C 5.0582526996 -1.1914544465 3.6250564731
 H 5.4563020009 -3.3000225588 3.834803888
 H 4.5037842782 0.83206493 3.1182360644
 H 5.5744891144 -0.913616777 4.539828087
 C 3.1201448452 3.4853139491 -1.6934326207
 C 3.2327505861 3.2080675432 -3.2099817537
 C 4.411300106 3.0569367337 -0.938382624
 H 2.9790212392 4.5675344324 -1.5637720561
 H 2.2468595365 3.3182794484 -3.6731779255
 H 3.5313883974 2.1608179235 -3.3581514444
 H 4.2318039103 2.116991652 -0.3983563752
 H 5.1878188184 2.816575379 -1.6732284664
 C 4.2204866459 4.1359644672 -3.9266620249
 H 5.2365641463 4.051903273 -3.5236869333
 H 4.2709549276 3.8977042279 -4.9951828183
 H 3.9121576033 5.184661265 -3.8334743946
 C 4.969935149 4.108405308 0.0279189891
 H 5.8745195426 3.7411228609 0.5262065331
 H 5.2330254967 5.0282880031 -0.5079389703
 H 4.2474947907 4.3803239198 0.8053579918

TS C-C *R,S*

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.64094002 A.U.

B3LYP / 6-31+G(d,p)

SCF Done: E(RB3LYP) = -2990.82947208 A.U.

0 1

C 0.4933528397 -2.1941747504 -1.9608738936
 C 0.3932258432 -1.2898299145 -0.8088259182
 C 1.7853148956 -1.0479660972 -0.7958387063
 C 1.9999248021 -1.9858765955 -1.9405265434
 O 2.9496318092 -2.390362741 -2.5858987779
 O -0.3162379393 -2.8135772759 -2.6506226962
 N 2.5568864888 -0.2414451314 -0.0499579544
 N -0.6562311317 -0.8427096868 -0.085168238
 H 2.074400658 0.3171843682 0.6530128144
 H -0.4291697956 -0.3019732797 0.7514688177
 C -1.9325452235 -1.5782714761 -0.1022005054
 C -2.0633143035 -2.4800642009 1.1314111455
 C -1.9941071987 -3.9087642492 1.0489440875
 C -2.2202777358 -1.907628744 2.3807501618
 C -1.8167391544 -4.6343495776 -0.1639156794
 C -2.1159827093 -4.6376788158 2.2813036107
 C -2.3195463245 -2.7242457644 3.5276321486
 H -2.2630802019 -0.8298662252 2.5064720813
 C -1.7686310929 -6.0168451375 -0.1520033917
 H -1.6763151187 -4.1064382404 -1.097206383

C -0.2868557075 5.8401259141 2.7219909653
 C -0.6121837645 6.5244340395 1.581699694
 H -0.4787538041 6.2588395563 3.7049024318
 H -1.0730515976 7.5065930906 1.6189910484
 O -0.7289034918 6.7195150455 -0.7471044772
 N 0.6082085245 3.9390660855 3.8427980892
 C -0.4698189086 6.2386280256 -2.066834806
 H -0.8608062275 7.0018135221 -2.7409255332
 H -0.9713877225 5.2833524614 -2.254508139
 H 0.6076064295 6.1175604778 -2.234255931
 C 3.0258953759 1.2645441012 -2.472013951
 C 3.7255953937 2.6428613236 -2.5405593839
 H 3.3876960018 0.573500673 -3.2361145446
 C 2.9977034494 1.5190465479 0.029306739
 C 4.8175062883 0.2890492422 -1.0818566858
 C 4.7168897058 2.7627490432 -1.3665074367
 H 2.9832754452 3.4468354962 -2.4929266147
 H 4.2493151591 2.7448599271 -3.4960180161
 H 3.2389117101 0.9122612882 0.9024369877
 C 3.9216323535 2.7707205952 -0.0463446325
 C 5.669554104 1.5378539868 -1.4214481784
 H 5.0005046988 -0.0791987946 -0.0707407352
 H 4.9739782669 -0.5409801769 -1.7703102523
 H 5.2953399539 3.6867676613 -1.4553532112
 H 4.5929994437 2.7927160034 0.8165032829
 H 3.3200812269 3.6838777802 0.0053226447
 H 6.0354922164 1.4512569157 -2.4515279305
 H 1.3166153368 2.5747392304 -0.7841983503
 N 3.3404368306 0.6225496021 -1.1461560575
 C 6.867695356 1.6500272589 -0.5146253957
 C 8.1322818304 1.6784358048 -0.9380487194
 H 6.6635621524 1.7070300814 0.5553309687
 H 8.9638048025 1.767990564 -0.2443263563
 H 8.3840776284 1.6127394946 -1.9948305999
 C 2.3259694351 -3.074128366 -1.0224064845
 O 2.9946346618 -1.9631651187 -0.9026693388
 C 4.4969642553 -5.8096639089 1.9607915724
 C 3.2937497576 -5.4338517736 1.3715420389
 C 2.9015872566 -4.0853963221 1.3541468159
 C 3.7580390888 -3.1339393549 1.9399478295
 C 4.979284096 -3.5135134092 2.5210868534
 C 5.3476229086 -4.8513868992 2.5351845205
 H 4.7805568803 -6.8585722793 1.9754127146
 H 2.6485327131 -6.1841771109 0.9224683761
 C 1.7038755928 -3.6103572162 0.6465206404
 C 3.3465598148 -1.732232525 1.9683929611
 H 5.6120793208 -2.7499943987 2.961783173
 H 6.2846968446 -5.1562758856 2.9909287667
 C 1.126908203 -2.3774527575 1.1503045552
 O -0.0235575734 -1.9818054316 1.0156759701
 O 2.0028022088 -1.4666537465 1.7169960443
 O 4.0343246489 -0.7789659397 2.2825857498
 H 1.9434123588 1.3438016799 -2.5712446261
 H 2.8656430891 -0.3302395267 -1.0585211346
 H 2.9516487014 -3.9751975523 -1.2030119737
 H 0.9454566379 -4.3677892155 0.4685697815
 H 1.3944301361 2.265338701 4.7375972818
 C -3.8563680827 -0.8667617108 0.036947448

C -2.0650310592 -6.0597787763 2.2481738316
 C -1.8991595713 -6.7353265406 1.0689968279
 H -2.1615723861 -6.5878113577 3.1916039071
 H -1.8581886336 -7.819592847 1.0351534638
 O -1.5955008296 -6.7975274409 -1.2503732128
 N -2.277591707 -4.0426325602 3.4964267587
 C -1.4978636303 -6.1619991545 -2.5256462861
 H -1.3553708885 -6.9678089106 -3.2468482492
 H -0.6505366138 -5.469483867 -2.5681341165
 H -2.4196082388 -5.6159871909 -2.7618266817
 C -2.7784929775 -0.1707113571 -2.6414669637
 C -3.8926607864 -1.1970519691 -2.9529459509
 H -2.7776570363 0.673476283 -3.3342468588
 C -3.1687702156 -0.6518056082 -0.2067945227
 C -4.2800639268 1.2499623841 -1.3030016071
 C -5.0131583626 -1.0556941921 -1.9029110741
 H -3.4860970601 -2.2140329578 -2.9370289337
 H -4.2865170379 -1.0233939974 -3.9590845754
 H -3.2848502342 -0.0831560263 0.7166518888
 C -4.4587102633 -1.4652663734 -0.5239089383
 C -5.4620048221 0.4317225894 -1.8849868645
 H -4.4578346624 1.5675225332 -0.2735023359
 H -4.0449673757 2.1384144638 -1.8893298952
 H -5.8602576612 -1.6954965043 -2.1664618388
 H -5.2047993156 -1.3082645257 0.2598921071
 H -4.2338993188 -2.5366568751 -0.5277424138
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 H -6.7098860505 0.4698820953 -0.0498494014
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 O -3.7328259241 1.9996461349 2.0891924228
 H -1.7862108289 -0.6200454902 -2.6579970514
 H 0.9560702869 3.687567235 1.167440991
 H 0.3292929763 2.4001831307 -0.7895336443
 H -2.2500811683 1.1232347655 -1.0159773991
 H -2.4441560035 -2.2605828577 4.505051365
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 H 1.1875014742 -5.264240446 -1.5956723693
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TS acylation *R,R*

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.63329880 A.U.

B3LYP / 6-31+G(d,p)

SCF Done: E(RB3LYP) = -2990.81998104 A.U.

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 C 4.1645759508 0.6217574309 -2.2605849973
 C 6.2067900111 0.2549533314 -1.0456704404
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 H 3.0850379014 0.5878462559 -2.3338246953
 C 6.941705793 0.766005256 -2.1136280751
 H 6.72875509 -0.0685456922 -0.1499525855
 C 6.2892467231 1.2131459143 -3.2658196734
 H 4.3746995713 1.4934538109 -4.2156057233
 H 8.0245046709 0.8224469851 -2.0408706309
 H 6.8592973333 1.6168478993 -4.0980399508
 C 4.334589284 -1.8644176439 0.4401783313
 C 3.6495669344 -2.4685340109 1.5093574615
 C 5.2250289374 -2.648197754 -0.2996644594
 C 3.864743595 -3.8046478454 1.8401479522
 H 2.9400186666 -1.8851548189 2.0893817132
 C 5.444137222 -3.9893123885 0.0310838615
 H 5.7410094869 -2.2266946035 -1.1529125832
 C 4.7700441811 -4.5725508848 1.1020153678
 H 3.3233303545 -4.2458345537 2.6726434542
 H 6.139033755 -4.5770633522 -0.5626683662
 H 4.93934063 -5.6153027186 1.3563988818
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 C 5.213172838 0.1445813421 2.3722215173
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 H 3.377632612 2.246253823 0.4385629027
 C 5.1124247024 2.3563346882 3.3584752449
 H 6.1939306437 0.695028601 4.205515009
 H 3.9636933579 3.8089064969 2.2486415744
 H 5.3830428891 3.0484481429 4.1510118018
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 C -1.5791758075 5.2492538854 -1.5094496652
 C 0.3479696887 4.1289875712 -2.7403111677
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 H -2.180463857 5.1598515489 -0.6006589467
 H -2.1812134628 4.7958134117 -2.3075183282
 H -0.2005829089 3.2879527304 -3.1881420282
 H 0.1802277431 4.9861896637 -3.4049720703
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 H -0.753573869 6.8823192092 -2.7248588265
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 H -0.8167339801 7.2260256723 -0.9901560765
 C 1.8490012269 3.8231005146 -2.7130092663
 H 2.226836493 3.6058039795 -3.7190386414
 H 2.4152096346 4.6780757212 -2.3226315515
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TS acylation *R,S*

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.63783578 A.U.

B3LYP / 6-31+G(d,p)

SCF Done: E(RB3LYP) = -2990.82542357 A.U.

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 C -1.9137916875 0.3085534032 -0.6764135254
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 O -3.4376566909 1.3761379938 -2.3852462887
 O -0.3804941567 2.5845779515 -2.5394871476
 N -2.4656669477 -0.6268909696 0.1050446727
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 H -2.7864312545 2.4722578871 1.8147809727
 C -5.3064705775 4.2720676578 -0.4955455998
 H -5.6347611172 2.3580783382 -1.4026495589
 C -4.6113300182 5.0014434684 0.4675203737
 H -3.1456285334 4.8962281954 2.0504309074
 H -6.0094407068 4.7715227077 -1.1568114553
 H -4.7714800035 6.0714018822 0.5685797953
 C -4.4442351884 -0.0389544279 1.3875925485
 C -5.209516995 0.5850712214 2.3786559855
 C -4.170016861 -1.4102516115 1.5230738337
 C -5.6720215649 -0.1366263238 3.4841643918
 H -5.4528586902 1.6376629674 2.2969545265
 C -4.6209971872 -2.1278189146 2.6286207169
 H -3.61170311 -1.9258693718 0.7471513633
 C -5.3754870322 -1.4915701842 3.6180478694
 H -6.2653292449 0.3704003018 4.2402228035
 H -4.3904219905 -3.1863243569 2.7127653264
 H -5.7324314327 -2.0498591615 4.4790193565
 C 0.0338353536 -4.0621193732 -1.5936275295
 C 0.9529440582 -3.8950483199 -2.8214942179
 C -1.4701068797 -4.0678281826 -1.9839662346
 H 0.2860113851 -5.0250530477 -1.1271414825
 H 1.986005222 -3.8403285582 -2.4638899048
 H 0.7356031129 -2.9279726108 -3.3016841886

H 3.2359809985 -1.7976161075 -3.0492302071
 H 3.158039406 -3.3915684633 -3.7666646432
 C 1.7988945493 -1.95828969 -4.6529564496
 H 2.5045990861 -1.6541959244 -5.4349920215
 H 1.1076407542 -2.6817922251 -5.1003719744
 H 1.2115407764 -1.0755944765 -4.3711957805
 C -0.6560000548 -4.2894392921 -2.4484166767
 H -1.1426965604 -3.4988828506 -3.0323256578
 H -1.1223386754 -5.242032642 -2.7266566265
 H -0.8798831468 -4.0945945546 -1.3945942107

Figure S5 Binding mode B

PreTS RR

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.65281331 A.U.

B3LYP / 6-31+G(d,p)

SCF Done: E(RB3LYP) = -2990.84397878 A.U.

0 1
 C 0.7336831895 1.9362491692 -2.1640138734
 C 0.4989555584 1.1880012618 -0.9336352428
 C -0.8619720447 1.5690851361 -0.8696577239
 C -0.7174141225 2.3860251533 -2.1216460446
 O -1.4264437099 3.1076743496 -2.7975994173
 O 1.7106058964 2.1280762081 -2.8937874425
 N -1.8047092101 1.3169821188 0.0415171896
 N 1.2989116837 0.4015385756 -0.1721101934
 H -1.5370334576 0.6539721993 0.7781953641
 H 0.8848704395 0.0729925537 0.7078473265
 C 2.7578134304 0.6053277401 -0.1966070562
 C 3.2302830731 1.3931545817 1.0264009317
 C 3.6365486399 2.7640528117 0.9321091085
 C 3.2330290356 0.798082031 2.2743932528
 C 3.6646118293 3.5109192478 -0.2805696611
 C 4.0371083517 3.4072957442 2.1528477667
 C 3.6413175842 1.5302793925 3.4098412913
 H 2.9179354076 -0.2320534371 2.4120025997
 C 4.0744453327 4.832373884 -0.2789330997
 H 3.3350531557 3.0605323065 -1.2072649723
 C 4.4569957304 4.7666750118 2.1091759296
 C 4.478377432 5.4632387068 0.9309201963
 H 4.7568579641 5.230325642 3.0435816605
 H 4.7947498107 6.5007616043 0.8889735525
 O 4.1287638116 5.6298701499 -1.3763138753
 N 4.0377034748 2.7875766484 3.3662335487
 C 3.7862405162 5.0672824512 -2.6438968767
 H 3.8895932426 5.879337098 -3.3645406563
 H 2.7580907839 4.6901842323 -2.6544739914
 H 4.4702793054 4.2515505654 -2.9076592603
 C 3.371234285 -0.9073423938 -2.8364320855
 C 4.9080394407 -0.7690911944 -2.9305336201
 H 2.9559753816 -1.5708504186 -3.5968944158
 C 3.5059500434 -0.7386931284 -0.3107307531
 C 3.6043106643 -2.934260752 -1.4364909129
 C 5.5512820347 -1.3699069345 -1.6659051396
 H 5.1849105338 0.2854509324 -3.0246234485
 H 5.2759630041 -1.2816907249 -3.8245090533
 H 3.2498443891 -1.3666600901 0.5458488284

H -2.040711593 -3.4191187403 -1.3060262671
 H -1.5870288521 -3.6119529803 -2.9765858654
 C 0.8364649049 -5.0132026813 -3.8632090785
 H -0.1638037032 -5.061825061 -4.3082541398
 H 1.5503697144 -4.8566279806 -4.6805915027
 H 1.0513066397 -5.9927553066 -3.418207695
 C -2.1230572645 -5.4559106964 -1.9866607856
 H -3.177307678 -5.3954842807 -2.2814989078
 H -1.6195933117 -6.1369893496 -2.6813341309
 H -2.0804148282 -5.9138291832 -0.9910023875

PreTS RS

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.65350504 A.U.

B3LYP / 6-31+G(d,p)

SCF Done: E(RB3LYP) = -2990.84535715 A.U.

0 1
 C -0.5293944177 1.8686293948 2.1357163105
 C -0.3391289282 1.2012106329 0.8519075059
 C 1.051769214 1.4674369971 0.8370889043
 C 0.9536151283 2.191527256 2.1464316996
 O 1.7097789647 2.7876066864 2.8927292455
 O -1.4997356441 2.0789876862 2.8711823974
 N 1.9822882337 1.2015537859 -0.083651925
 N -1.1796939863 0.5539590758 0.0188922418
 H 1.6800244321 0.576340806 -0.8421963222
 H -0.7798684265 0.2129824164 -0.861551596
 C -2.6333308673 0.7444818728 0.0996591604
 C -3.1394918174 1.6059641295 -1.0596900807
 C -3.4808959947 2.98591194 -0.8769177793
 C -3.2287128537 1.0777271984 -2.3342305912
 C -3.4156033408 3.669328558 0.3712341183
 C -3.9127480805 3.7073480185 -2.0418154962
 C -3.6601897748 1.8842347259 -3.4095623405
 H -2.9661099119 0.0446177934 -2.5411725415
 C -3.7675859782 5.0048616398 0.4559788951
 H -3.0605195995 3.1580255866 1.2563471064
 C -4.2706285561 5.0785008968 -1.9093854522
 C -4.2030873423 5.7134942625 -0.6985821617
 H -4.5959404704 5.6013463009 -2.8031227894
 H -4.4718339768 6.7594631036 -0.5889248384
 O -3.733780209 5.7469397154 1.5925276569
 N -3.9995246541 3.1523985898 -3.283317132
 C -3.3598581154 5.1062566999 2.8132517862
 H -3.3930321208 5.8844564408 3.5766890381
 H -2.3511275066 4.6841006285 2.7564870189
 H -4.0675342687 4.3085200402 3.0693622826
 C -3.1867131272 -0.913208626 2.666012764
 C -4.7193460409 -0.7558340403 2.7911310225
 H -2.7754245922 -1.6256382967 3.3836721159
 C -3.3730113316 -0.6107967534 0.1538954395
 C -3.4590689589 -2.8620316944 1.1664694338
 C -5.3926516698 -1.3058539704 1.5191560486
 H -4.978988368 0.2991726775 2.9238446789
 H -5.0788235818 -1.2918369673 3.674597196
 H -3.1229795534 -1.1889359492 -0.7388510715

C 5.045095993 -0.5869603355 -0.4394716062
 C 5.1521500372 -2.8692747321 -1.5773577823
 H 3.2907422898 -3.356983134 -0.4790369385
 H 3.133963518 -3.5128529936 -2.2326508508
 H 6.6399936243 -1.290573434 -1.7276546364
 H 5.5280257102 -0.9306300668 0.4785680338
 H 5.3098380291 0.4692917796 -0.5554060252
 H 5.4335574439 -3.3374257779 -2.5270498807
 H 2.9700326255 1.1788211735 -1.0963115986
 N 3.0175737845 -1.5419848559 -1.5065586028
 C 5.8440931267 -3.6199229741 -0.4675818269
 C 6.7219594101 -4.604777046 -0.6621367252
 H 5.5956528436 -3.3221670459 0.5519491968
 H 7.204376962 -5.109906663 0.1699961235
 H 6.9922078463 -4.9426562605 -1.6606597886
 C -0.2697568895 -3.3028259265 -1.5305336143
 O 0.4708711187 -2.5134318399 -2.1030025528
 C 0.6434537162 -4.0734337936 5.2531718504
 C -0.3338271758 -4.5341186236 4.397228947
 C -0.8609964666 -3.7041159095 3.3618002516
 C -0.3189351541 -2.3846421827 3.2552987568
 C 0.6768415696 -1.9305815485 4.1496208913
 C 1.1614262124 -2.7588107178 5.1413484211
 H 1.0212413371 -4.7301375806 6.0335387888
 H -0.723231686 -5.5436026975 4.5039800899
 C -1.867091177 -4.1391217447 2.4741349212
 C -0.8086374117 -1.5205669208 2.2134102905
 H 1.039917423 -0.9130388542 4.0405127183
 H 1.9231967667 -2.4110389654 5.8325421651
 C -2.3855505435 -3.3062908194 1.4787607266
 O -3.2657863333 -3.4976392875 0.6365760809
 O -1.777658067 -1.9928461136 1.39642881
 O -0.4047592101 -0.3593865088 1.9892782154
 H 2.8484426224 0.0481360936 -2.9046605663
 H 1.9834772345 -1.6531821603 -1.4706597677
 C -1.3944491355 -4.0642923937 -2.1766859077
 H -0.1310905716 -3.5009001402 -0.4500999578
 H 3.6416130752 1.0490150928 4.3865470159
 C -3.2472006457 1.6732151489 -0.0584088906
 C -3.8219825219 0.9247732326 -1.2881443201
 C -4.1507924889 1.573323294 -2.4839695781
 C -3.9345888928 -0.4760521804 -1.2358584433
 C -4.6121467417 0.8499461437 -3.5884134207
 H -4.025575569 2.6445920499 -2.5711205665
 C -4.4011208433 -1.1951391267 -2.3353562257
 H -3.6607094598 -1.0208217637 -0.3374256101
 C -4.7483111109 -0.5351704584 -3.5176205334
 H -4.8615224098 1.3787127372 -4.5046668636
 H -4.4982501319 -2.2747726151 -2.2604428493
 H -5.1151152926 -1.0965600294 -4.3729430383
 C -3.4460460926 3.2098702057 -0.0925753382
 C -4.723434689 3.7378571438 -0.341416518
 C -2.4205182271 4.0996115079 0.2468018268
 C -4.9573779617 5.1108600874 -0.2882260193
 H -5.547019795 3.0707767345 -0.5753524821
 C -2.6539157898 5.4765115834 0.3050866427
 H -1.4297354043 3.7261207988 0.478038133
 C -3.9204565307 5.9904650713 0.0326277127
 C -4.9112289645 -0.4767190969 0.3134161719
 C -5.0002235049 -2.8015666959 1.364222496
 H -3.1783968402 -3.2295570527 0.1772041782
 H -2.9684648701 -3.4893125131 1.9123036892
 H -6.4794149576 -1.2256087361 1.6082598053
 H -5.4081280754 -0.7910242824 -0.6077353308
 H -5.1807372903 0.5726372883 0.4715535542
 H -5.248669806 -3.3008861783 2.3073750259
 H -2.8235307867 1.2628066853 1.0373110389
 N -2.8620914544 -1.4779656612 1.2985299986
 C -5.7324584475 -3.5159618872 0.2562986686
 C -6.6075772635 -4.5030819319 0.4520727442
 H -5.518386007 -3.1897937985 -0.762256113
 H -7.1208650006 -4.9812569666 -0.3774745513
 H -6.8447991396 -4.8695503091 1.4489212116
 C 0.6937477378 -3.056713736 1.4772314218
 O -0.1284411564 -2.2017595522 1.1746844236
 C -1.1707230537 -3.8654735865 -5.2625225845
 C -0.2144145878 -4.4538917876 -4.4629289576
 C 0.4811846727 -3.7032511525 -3.466843335
 C 0.1288911839 -2.3230874578 -3.3375698552
 C -0.848465194 -1.7389303271 -4.1741475361
 C -1.4992380439 -2.4932298269 -5.1297272524
 H -1.6795281129 -4.4647442819 -6.01422288
 H 0.0280946897 -5.5067776024 -4.584892833
 C 1.4659560084 -4.2712685855 -2.6327231854
 C 0.7932128508 -1.5322077527 -2.3328440582
 H -1.06219177 -0.6812235438 -4.0526702218
 H -2.246273252 -2.0447398767 -5.7777063782
 C 2.1446115093 -3.5176005959 -1.6705302526
 O 3.0158003971 -3.8352068968 -0.8583864445
 O 1.7534467168 -2.1237392614 -1.5899624119
 O 0.5511591732 -0.3306004956 -2.0895863392
 H -2.6476549926 0.0286437432 2.7813408851
 H -1.8314915724 -1.5916027922 1.2240640237
 C 0.4152681437 -4.2831636146 2.3065218835
 H -3.7287990485 1.4544845945 -4.4076803385
 C 3.4465768495 1.4344243207 0.0453742114
 C 3.9631308288 0.5014382331 1.1704423705
 C 4.272156218 0.9653437812 2.4545582746
 C 4.0242851282 -0.8816596375 0.9291110779
 C 4.6680691681 0.0775928114 3.4601508055
 H 4.1807991301 2.0187586247 2.6854457521
 C 4.4221507976 -1.7663907057 1.9305694014
 H 3.7546694492 -1.2844401902 -0.0412417741
 C 4.7545199877 -1.2898151013 3.2019890789
 H 4.9059787992 0.4641034264 4.4477981788
 H 4.4711450242 -2.8283257114 1.7058218853
 H 5.0710689456 -1.9775931608 3.981842038
 C 3.7604417508 2.9365264172 0.2607936833
 C 5.0581926071 3.3330068677 0.6215654794
 C 2.8241653364 3.9355022158 -0.0313937948
 C 5.3962698505 4.6817278779 0.7229637579
 H 5.816366363 2.5830709905 0.8224130854
 C 3.161409866 5.2877631998 0.0680200652
 H 1.8229835372 3.6669357863 -0.3478623253
 C 4.4464480767 5.6689722481 0.4509531326
 H 6.4066421746 4.9592659781 1.01145512

H -5.9544308935 5.491809169 -0.4927712785
 H -1.8373838725 6.1442722794 0.5667835894
 H -4.1014014279 7.0609523293 0.0757917399
 C -3.9144086922 1.2266372287 1.2707688498
 C -3.2467058652 1.4186388546 2.4901679879
 C -5.2296233994 0.7447672811 1.3043074991
 C -3.8623166095 1.1041408956 3.7019105429
 H -2.2391062642 1.8207412409 2.5025606233
 C -5.8501082897 0.4397063721 2.5175200923
 H -5.7767504142 0.5961329733 0.3802595047
 C -5.1683236859 0.6117566877 3.7221714573
 H -3.3187572374 1.251788593 4.6311684293
 H -6.8686020831 0.0608879082 2.51462025
 H -5.6489888925 0.3680643505 4.6656087129
 H -2.2891380087 -5.1340844255 2.5619796425
 H -2.2855008453 -3.7111233513 -1.6296938854
 C -1.5147961399 -3.7312341526 -3.6729640383
 C -2.6913648561 -4.3945960242 -4.3958448233
 H -0.5766728932 -4.0100851731 -4.1711492162
 H -1.598080726 -2.6427724586 -3.77418567
 H -2.7456048842 -4.0429217296 -5.4323425346
 H -2.59463551 -5.4852180358 -4.4246951562
 H -3.6464275785 -4.1556153938 -3.9132209963
 C -1.2322144567 -5.5773272459 -1.8329969892
 C -2.5498723963 -6.2914681275 -1.5076435045
 H -0.568157808 -5.6855721726 -0.9638790632
 H -0.716375066 -6.0714476359 -2.6668185456
 H -2.3654274798 -7.3407147036 -1.2489262921
 H -3.0406718565 -5.8057518155 -0.6576902939
 H -3.2448176788 -6.2730308088 -2.3529076488
 H 2.4121544262 6.0416165202 -0.1588175101
 H 4.7084993709 6.7204945096 0.5297237874
 C 4.0809102674 1.102200586 -1.3322677705
 C 3.4041684397 1.4176573612 -2.5198722969
 C 5.3860396309 0.599353789 -1.4271119142
 C 4.0016210465 1.2059064786 -3.7633238048
 H 2.403549559 1.8344123356 -2.4834456416
 C 5.9876146351 0.3962619318 -2.6701324044
 H 5.9392222217 0.3536482046 -0.5274062312
 C 5.2967873007 0.6929631673 -3.8455530159
 H 3.4507719807 1.4485703865 -4.6680372441
 H 6.9981762497 -0.0008110675 -2.7149424362
 H 5.7625653379 0.5286567043 -4.8133199145
 H 1.7313320024 -5.3187993243 -2.7234715226
 H -0.6255584805 -4.2311594394 2.6549311059
 C 0.5824458727 -5.5160149395 1.3757765017
 C 0.2080258249 -6.8494108754 2.0321279572
 H 1.6158346434 -5.5480847139 1.0090349362
 H -0.0482004794 -5.3678097632 0.4893512603
 H 0.2732807771 -7.6610518037 1.2992851983
 H 0.8740590033 -7.103668172 2.8629881462
 H -0.8187277271 -6.8286641363 2.4174595978
 C 1.3631059676 -4.310227082 3.5281889762
 C 1.1586710484 -3.1345382658 4.4908162495
 H 2.4026367133 -4.325745403 3.1735193175
 H 1.2073299122 -5.2507440084 4.0675457991
 H 1.8177609913 -3.2272391266 5.3606258225
 H 1.3775211015 -2.1720500333 4.0138622029
 H 0.1254816354 -3.0988455524 4.8574926143
 H 1.7255950405 -2.9642762738 1.0964384192

min02 – RR

B3LYP / 6-31G(d)
 SCF Done: E(RB3LYP) = -2990.66062796 A.U.
 B3LYP / 6-31+G(d,p)
 SCF Done: E(RB3LYP) = -2990.84855142 A.U.

0 1
 C -0.0512775178 1.9464049614 -1.9548995573
 C -0.0554676502 1.2809789878 -0.646068702
 C -1.4626620909 1.1266445184 -0.6618373576
 C -1.5642345205 1.8353766675 -1.9724514977
 O -2.45214818 2.197265302 -2.7262683694
 O 0.8171959243 2.4040806499 -2.6975753602
 N -2.3057433492 0.6115221452 0.2494622668
 N 0.9231923174 0.9511212657 0.2121827245
 H -1.8742414565 0.0703371456 0.9980297533
 H 0.6553333253 0.5212542903 1.0945424099
 C 2.2663807859 1.5466244753 0.1271412919
 C 2.4181240805 2.6326911273 1.1986542711
 C 2.4018659904 4.0310811526 0.8829015083
 C 2.5302519846 2.2761723759 2.5298837172
 C 2.2723401808 4.5498387649 -0.4375567629
 C 2.5262749783 4.9508014349 1.9797469206
 C 2.637123959 3.266324828 3.5296129561
 H 2.5375393415 1.2335492656 2.8334912103
 C 2.2731751218 5.9159189779 -0.6561531474
 H 2.1339497633 3.8774925178 -1.273554294

H 2.4121544262 6.0416165202 -0.1588175101
 H 4.7084993709 6.7204945096 0.5297237874
 C 4.0809102674 1.102200586 -1.3322677705
 C 3.4041684397 1.4176573612 -2.5198722969
 C 5.3860396309 0.599353789 -1.4271119142
 C 4.0016210465 1.2059064786 -3.7633238048
 H 2.403549559 1.8344123356 -2.4834456416
 C 5.9876146351 0.3962619318 -2.6701324044
 H 5.9392222217 0.3536482046 -0.5274062312
 C 5.2967873007 0.6929631673 -3.8455530159
 H 3.4507719807 1.4485703865 -4.6680372441
 H 6.9981762497 -0.0008110675 -2.7149424362
 H 5.7625653379 0.5286567043 -4.8133199145
 H 1.7313320024 -5.3187993243 -2.7234715226
 H -0.6255584805 -4.2311594394 2.6549311059
 C 0.5824458727 -5.5160149395 1.3757765017
 C 0.2080258249 -6.8494108754 2.0321279572
 H 1.6158346434 -5.5480847139 1.0090349362
 H -0.0482004794 -5.3678097632 0.4893512603
 H 0.2732807771 -7.6610518037 1.2992851983
 H 0.8740590033 -7.103668172 2.8629881462
 H -0.8187277271 -6.8286641363 2.4174595978
 C 1.3631059676 -4.310227082 3.5281889762
 C 1.1586710484 -3.1345382658 4.4908162495
 H 2.4026367133 -4.325745403 3.1735193175
 H 1.2073299122 -5.2507440084 4.0675457991
 H 1.8177609913 -3.2272391266 5.3606258225
 H 1.3775211015 -2.1720500333 4.0138622029
 H 0.1254816354 -3.0988455524 4.8574926143
 H 1.7255950405 -2.9642762738 1.0964384192

min02 – RS

B3LYP / 6-31G(d)
 SCF Done: E(RB3LYP) = -2990.64777924 A.U.
 B3LYP / 6-31+G(d,p)
 SCF Done: E(RB3LYP) = -2990.83700883 A.U.

0 1
 C -0.2455666278 1.8271323665 -1.9751536307
 C -0.2774732227 1.1769947063 -0.6582316156
 C -1.6671609157 0.9202780714 -0.7535072608
 C -1.7405600649 1.5988603542 -2.0816519272
 O -2.6009872075 1.8700709732 -2.9044303366
 O 0.6297761739 2.3367033446 -2.6739945229
 N -2.5154613427 0.3577686471 0.126647535
 N 0.6722402067 0.9311657898 0.2553620651
 H -2.077802783 -0.1543101532 0.8912234275
 H 0.4017352767 0.4490836684 1.1092006686
 C 1.9464559934 1.6645721782 0.2575126154
 C 1.8835118874 2.7967151403 1.2924841434
 C 1.8001647277 4.1790188219 0.9232599213
 C 1.8637156932 2.4902703012 2.640868602
 C 1.7859939145 4.6464041193 -0.4225002844
 C 1.727924654 5.1384000618 1.9905754071
 C 1.7786431808 3.514841829 3.60705889
 H 1.911602063 1.4604267298 2.9830878182
 C 1.7096766255 6.0008233606 -0.6927653274
 H 1.793464856 3.9405440969 -1.2416130226

C 2.5267192768 6.3484791442 1.7103386175
 C 2.4064153422 6.8229735496 0.4317201294
 H 2.6243494231 7.0231386843 2.5551515455
 H 2.404328977 7.8872214085 0.2174763127
 O 2.1482880678 6.5091055264 -1.8722836995
 N 2.6429711226 4.5619248554 3.2808771212
 C 2.0566591394 5.6744210058 -3.0279819049
 H 1.9542605706 6.3539225328 -3.8751177856
 H 1.1895972085 5.0076334018 -2.9773915436
 H 2.9649149166 5.0711417641 -3.1477232776
 C 3.4255177876 -0.1077323471 -2.1661423718
 C 4.7926532433 0.6145000451 -2.3417465356
 H 3.3508431181 -0.9816563452 -2.820667742
 C 3.3959283688 0.4920166342 0.2241783219
 C 4.3132597256 -1.6074625874 -0.5018743266
 C 5.5913742219 0.4732515965 -1.0315401449
 H 4.644059613 1.6766934759 -2.5701976598
 H 5.3544787704 0.1825583246 -3.1779972344
 H 3.3173026608 -0.0062251004 1.1965375502
 C 4.7999566662 1.1694094474 0.0912618743
 C 5.7562017828 -1.0407900056 -0.7301438291
 H 4.1875884919 -1.9520938089 0.5304481582
 H 4.1399187215 -2.4669418239 -1.1567355742
 H 6.5772592959 0.9386064404 -1.1354651725
 H 5.3389667304 1.1271571584 1.0429369511
 H 4.6968805251 2.2320686485 -0.1576729834
 H 6.1843465585 -1.507804404 -1.6262132651
 H 2.3230728469 2.0034393356 -0.8582127706
 N 3.2528092787 -0.6046857906 -0.7754346133
 C 6.6731048692 -1.3401375315 0.4247408015
 C 7.8199407333 -2.0169691134 0.3326408112
 H 6.3533923071 -0.9788457846 1.4038013796
 H 8.4446221775 -2.2063458307 1.201792905
 H 8.178935678 -2.4063159223 -0.6184465378
 C 1.1674094062 -3.5091018313 -0.6001768335
 O 0.8833336363 -2.1325204769 -0.4650257542
 C 3.4417503425 -3.8101939739 3.3440342911
 C 2.6776982025 -4.3638705542 2.3146453218
 C 1.5028849638 -3.7335401146 1.8988319786
 C 1.11420341 -2.5399443427 2.5249158674
 C 1.8848045102 -1.9752910916 3.5508360673
 C 3.0492840986 -2.6166284217 3.9623070956
 H 4.3471188792 -4.3142747702 3.6692287935
 H 2.9949090103 -5.2866017143 1.8362706361
 C 0.6828475414 -4.2220113798 0.73398744
 C -0.1342026995 -1.8925552651 2.0953188513
 H 1.550990155 -1.0576476448 4.0243604586
 H 3.6464486574 -2.1967769367 4.7656819029
 C -0.781835796 -3.9302596293 0.9501709198
 O -1.7050708663 -4.6343642581 0.6325870504
 O -1.0849209303 -2.6956381502 1.5105418228
 O -0.435575323 -0.7283747586 2.294172478
 H 2.5885206587 0.5474127421 -2.4183546576
 H 1.703577239 -1.5783159309 -0.5957468186
 C 0.5321134751 -4.1110511035 -1.8785940704
 H 2.2519644244 -3.6817167505 -0.6388856254
 H 2.7262990824 2.9673499226 4.5731802396
 C -3.7665318284 0.3834327615 0.067742444
 C 1.6577949908 6.5231615141 1.6686279878
 C 1.6511995788 6.9480944694 0.3670794072
 H 1.6075009894 7.2286474451 2.4921562781
 H 1.5952860523 8.0020208955 0.1128241761
 O 1.6786636184 6.5449511693 -1.9376826221
 N 1.71943441 4.7992155877 3.3106007139
 C 1.7646384163 5.6689714481 -3.0627650683
 H 1.7062172437 6.3118514217 -3.9420802448
 H 0.9431111712 4.9449897752 -3.0744524359
 H 2.7189955671 5.1280274088 -3.0657733653
 C 3.4300516183 -0.00669555716 -1.8136233755
 C 4.6863620979 0.8975068322 -1.9875296664
 H 3.5217260956 -0.9256443489 -2.4018524478
 C 3.1800117848 0.7619753737 0.5043803798
 C 4.4274621322 -1.223804986 0.0089349338
 C 5.4283221101 0.9688923586 -0.6387679686
 H 4.3968158722 1.9073918538 -2.3025904124
 H 5.3480134098 0.4976221987 -2.7646666332
 H 3.1030187609 0.3409936075 1.5123909899
 C 4.4895186067 1.616153316 0.3948571392
 C 5.7890127035 -0.477078152 -0.2089370757
 H 4.2956653732 -1.4973945948 1.0616948898
 H 4.421129465 -2.1497325349 -0.5709575865
 H 6.3411687791 1.5658491476 -0.7391200763
 H 4.9753158174 1.7038576671 1.3719087562
 H 4.2625603601 2.6389105248 0.0722071691
 H 6.3225280886 -0.9461857709 -1.0457253026
 H 2.0391437838 2.0898637497 -0.7395298753
 N 3.2498794774 -0.4203974052 -0.3989543759
 C 6.6795926118 -0.5537205581 1.0010415362
 C 7.9046441459 -1.0839829241 1.0152022756
 H 6.2703875511 -0.1521555959 1.9300355978
 H 8.5045174334 -1.1164847175 1.9211156091
 H 8.3554399976 -1.5051546444 0.1182472127
 C 0.5787689853 -3.4843309429 -0.7346839653
 O 0.7553146742 -2.1044545269 -0.5039018077
 C 3.3180569793 -3.8770413589 3.1852955847
 C 2.5392320962 -4.4249183315 2.1634318878
 C 1.3630059144 -3.7906407062 1.7584226621
 C 0.9751399413 -2.6110744672 2.4163867189
 C 1.7621991475 -2.0483330472 3.4290163236
 C 2.9387070828 -2.6856429909 3.8134919266
 H 4.2246599563 -4.3872841304 3.4970244952
 H 2.8477275583 -5.3495709149 1.6865676964
 C 0.4630399269 -4.2919337654 0.6546354852
 C -0.3169442799 -1.9998501895 2.0647242477
 H 1.4270169275 -1.1417740598 3.9222801907
 H 3.5488909135 -2.2689453867 4.6086665631
 C -0.9699239642 -4.1189354283 1.0869154779
 O -1.8679426473 -4.907682302 0.9674007284
 O -1.2805688886 -2.8441355834 1.5664656065
 O -0.6394237811 -0.8418556876 2.2647978599
 H 2.5229814314 0.4970621611 -2.1559038023
 H 1.6917359215 -1.8047800611 -0.4197223561
 C 1.5448766023 -4.1179514056 -1.7715645255
 H 1.7656200811 3.2550366615 4.6647659462
 C -3.9493265379 0.0306774907 -0.1005316334
 C -4.0007683254 -1.1492321782 -1.1056101718

C -3.939681221 -0.6664280582 -1.0600887725
 C -4.2847021877 -0.3115330419 -2.3699402087
 C -3.630324719 -2.01107124 -0.7960880091
 C -4.3529557848 -1.2774439273 -3.3784599743
 H -4.4708228508 0.7255080047 -2.6166806729
 C -3.6979159082 -2.9753029014 -1.8008061418
 H -3.3325150422 -2.3150654863 0.201179591
 C -4.0684651569 -2.6135046379 -3.0988873246
 H -4.6261120343 -0.9758808287 -4.3862896159
 H -3.4593009212 -4.0077792332 -1.5619495945
 H -4.1288950471 -3.3643458798 -3.8824281637
 C -4.5104700249 1.7194487323 -0.1794451867
 C -5.8450965591 1.7081463074 -0.6141107775
 C -3.9365777613 2.9516181248 0.155585745
 C -6.5693927464 2.89268532 -0.7424845811
 H -6.3282217291 0.7666915969 -0.8545578313
 C -4.6609168087 4.1393060175 0.028869571
 H -2.9182482178 2.9938929931 0.5247205973
 C -5.978874093 4.1179326313 -0.4255957414
 H -7.5988081267 2.8546527837 -1.0888123731
 H -4.1875058324 5.0823191959 0.2891272987
 H -6.5416922945 5.0418731752 -0.5262271764
 C -4.3156442903 -0.1169900889 1.4310494857
 C -3.7871415966 0.3729005186 2.6347261389
 C -5.4263098071 -0.9705753994 1.4953010881
 C -4.331426847 -0.0031899402 3.8639387879
 H -2.9524045679 1.065867491 2.621222138
 C -5.975903069 -1.3409958015 2.7234766494
 H -5.8650492997 -1.3582767067 0.5825620719
 C -5.4281297564 -0.8640856183 3.9152780525
 H -3.8977772436 0.3862486821 4.7810869712
 H -6.8333952043 -2.0081773378 2.744371408
 H -5.8537320076 -1.1560743609 4.8713485293
 H 0.7786920511 -5.3023444023 0.6151587819
 H -0.558289009 -4.0355421113 -1.7667131378
 C 0.9169164132 -3.2605029818 -3.1075483371
 C 0.1237085061 -3.6140760957 -4.3706867143
 H 1.9944460254 -3.3753086785 -3.3023888939
 H 0.7489537758 -2.2059025641 -2.8682156711
 H 0.4307909411 -2.9816026273 -5.2114459161
 H 0.2686277728 -4.6577121432 -4.6740156614
 H -0.9500491137 -3.4573717404 -4.2110678733
 C 0.9206260307 -5.6072336593 -2.063299477
 C -0.2665503048 -6.5777601537 -2.0292513782
 H 1.650494296 -5.906282383 -1.2979986544
 H 1.4496058191 -5.7262166412 -3.0168220427
 H 0.0666817072 -7.615334187 -2.1491917381
 H -0.8167977218 -6.5018227122 -1.0849767527
 H -0.9735975771 -6.3581651705 -2.8380675901

Prod-RR

B3LYP / 6-31G(d)
 SCF Done: E(RB3LYP) = -2990.68506671 A.U.
 B3LYP / 6-31+G(d,p)
 SCF Done: E(RB3LYP) = -2990.87213220 A.U.

0 1

C 1.147303314 2.798824398 -1.6553319777

C -4.0590720247 -0.9257559113 -2.4887781674
 C -3.853051985 -2.4695380985 -0.6527977848
 C -4.0131620371 -1.9933128775 -3.3885075582
 H -4.1135510096 0.0877227184 -2.8680774522
 C -3.8044800513 -3.5366807195 -1.5512692323
 H -3.7705644288 -2.6752376119 0.408148843
 C -3.8955987236 -3.3043237268 -2.9254467921
 H -4.0665649872 -1.7933326404 -4.4555075157
 H -3.6935162792 -4.5474076711 -1.169257321
 H -3.868430386 -4.1347549544 -3.6259564278
 C -4.7333529649 1.2903171746 -0.544502427
 C -5.9488776507 1.1761787103 -1.233695739
 C -4.3232801456 2.5651044596 -0.1317125107
 C -6.7141004175 2.3053124431 -1.5287276353
 H -6.3059005453 0.201506363 -1.5485023709
 C -5.0862807184 3.6951863478 -0.4277652526
 H -3.4028181131 2.6809799731 0.4300310808
 C -6.2845327051 3.5725182207 -1.1322765921
 H -7.6487733902 2.1895535906 -2.0710685243
 H -4.7404392244 4.6730506102 -0.1032512457
 H -6.8785881279 4.4520650582 -1.3648128064
 C -4.5663205764 -0.3366098816 1.2759445176
 C -4.031549012 0.1507468921 2.4762702347
 C -5.7588434525 -1.0747026444 1.3357861396
 C -4.6519548181 -0.1169048516 3.6997431637
 H -3.1323094172 0.7564414128 2.4712337193
 C -6.3804385782 -1.3390526985 2.5551528287
 H -6.2063618419 -1.4523998629 0.4226100196
 C -5.8270020468 -0.8650994343 3.7469009856
 H -4.2115684694 0.2689926196 4.6151870469
 H -7.2996712615 -1.9183382945 2.5714653664
 H -6.3095810444 -1.0728695046 4.697884025
 H 0.6148525716 -5.3561953248 0.4653071272
 H -0.4196472754 -3.5470696031 -1.1791422744
 H 1.7068320917 -3.3134919692 -2.5046609163
 C 2.9210545819 -4.5399628759 -1.2188155418
 C 4.011122353 -4.6366818709 -2.2937492254
 H 2.8264914405 -5.5115972871 -0.7148768318
 H 3.2504712286 -3.8324405903 -0.4513235052
 H 4.9646742792 -4.9500371824 -1.8542761253
 H 3.7549618055 -5.3612308193 -3.0744009393
 H 4.1692077165 -3.6676996603 -2.7829419043
 C 0.8567160496 -5.2931305045 -2.5090641987
 C -0.1691366405 -4.8743909777 -3.5687364057
 H 0.3800175493 -5.9565130848 -1.77284037
 H 1.6280835586 -5.9015809461 -2.9950549705
 H -0.6088636329 -5.7555204547 -4.049717856
 H -0.9932784657 -4.2871717089 -3.1483000455
 H 0.3036226139 -4.2677332268 -4.3504807665

Prod-RS

B3LYP / 6-31G(d)
 SCF Done: E(RB3LYP) = -2990.67148060 A.U.
 B3LYP / 6-31+G(d,p)
 SCF Done: E(RB3LYP) = -2990.86229537 A.U.

0 1

C -0.2027291716 2.5645503024 1.9423360954

C 0.743048551 1.8258541764 -0.6366064546
 C -0.5869515564 2.3073898951 -0.6161985705
 C -0.2596509211 3.3729814427 -1.6081926614
 O -0.8502075489 4.296216646 -2.1423791337
 O 2.1832617171 3.0057713103 -2.292236387
 N -1.6532638287 1.8920017501 0.0805944419
 N 1.3598020237 0.8214757025 0.0061511544
 H -1.501700334 1.0186274748 0.6011267312
 H 0.7779540599 0.2698729242 0.6541453105
 C 2.7558950799 0.4504133428 -0.2328716702
 C 3.599499981 0.6364158063 1.0333773007
 C 4.3871556288 1.8184206036 1.2380070691
 C 3.5806853585 -0.3109314803 2.0398817302
 C 4.4943316005 2.8835681299 0.2978444032
 C 5.1090482805 1.9121820359 2.4764680289
 C 4.3248165924 -0.1073322241 3.2226393981
 H 3.0092970164 -1.2294275707 1.9563969306
 C 5.2899410908 3.9820674744 0.5745560655
 H 3.931338609 2.8553129052 -0.6263203963
 C 5.9140083292 3.0597405466 2.7211685241
 C 6.0073709801 4.067760907 1.7998774251
 H 6.4501901378 3.1054310155 3.6637780512
 H 6.6194880028 4.9465652434 1.9772491923
 O 5.4622492549 5.0470961664 -0.251154544
 N 5.0701169108 0.9563644184 3.4476241308
 C 4.8327209962 5.0232492472 -1.5329210281
 H 5.1099840793 5.961771484 -2.0148225731
 H 3.7436759303 4.9551504427 -1.4477998828
 H 5.1950400326 4.1792899401 -2.1320005818
 C 2.1438790356 -0.4658099949 -3.1266556982
 C 3.5473682127 -0.8412456323 -3.6639816312
 H 1.342909388 -0.7088027822 -3.827139177
 C 2.8826362617 -0.9968453672 -0.7757296691
 C 1.8918636854 -2.7487364055 -2.222569401
 C 4.1889753703 -1.8968837599 -2.7417528288
 H 4.1791520603 0.0514034602 -3.70570068
 H 3.4671103769 -1.2299565976 -4.6837598796
 H 2.607403739 -1.7098055009 0.0021694506
 C 4.2994476946 -1.3148016683 -1.3208894284
 C 3.2920148919 -3.1654754574 -2.7493897136
 H 1.6033211511 -3.2811149935 -1.3160560925
 H 1.1048486539 -2.8975987312 -2.9641211778
 H 5.1846766466 -2.1574338353 -3.1111473319
 H 4.806584515 -2.0115134389 -0.6489153141
 H 4.905868056 -0.4028671418 -1.3490426304
 H 3.1953885332 -3.481765725 -3.7942703289
 H 3.123494606 1.1253537254 -1.0045939366
 N 1.8728366545 -1.2731115899 -1.8804842937
 C 3.858709821 -4.3217879773 -1.9604421491
 C 4.4080566425 -5.4038908186 -2.5144570087
 H 3.7891168223 -4.2540429522 -0.87418935
 H 4.8128792426 -6.209640709 -1.9081738809
 H 4.4747338854 -5.5262279288 -3.5941437698
 C -0.9065198762 -4.2217322607 0.7023908796
 O 0.5590862142 -4.2534991504 0.6018978562
 C -0.725965227 -2.4256345161 5.1123827499
 C -1.3513118286 -2.3844215217 3.8654562625
 C -0.7041785789 -2.8913775431 2.7374398316
 C -0.1364529817 1.4984414083 0.9513132425
 C 1.2796371794 1.4266165489 1.0076577141
 C 1.3072630882 2.5067599313 2.0585885059
 O 2.1463748136 3.0779444961 2.7311209443
 O -1.1125619782 3.2266716243 2.4527291688
 N 2.150204692 0.7073273507 0.2999234573
 N -1.1159294595 0.8442371662 0.2691978024
 H 1.7230141747 -0.0877289277 -0.221228723
 H -0.7964515326 0.0824807627 -0.3410949278
 C -2.326062432 1.6107586508 -0.1010472333
 C -2.2260157722 2.1796112453 -1.5185226319
 C -1.9864550028 3.5721134601 -1.7599082996
 C -2.3213934798 1.3369384261 -2.6110401483
 C -1.8669401423 4.5553055137 -0.7357987815
 C -1.8656791992 3.9826959994 -3.1311941717
 C -2.1824736097 1.8523266331 -3.9178605429
 H -2.503758809 0.2726576418 -2.4944010117
 C -1.6375600677 5.8805248804 -1.0599213606
 H -1.9284539315 4.2686912255 0.3052396836
 C -1.6302709317 5.3562886987 -3.4212311569
 C -1.5194028182 6.2828028356 -2.4194530625
 H -1.542500225 5.6412610104 -4.4649398448
 H -1.3394567149 7.3320573531 -2.6317993128
 O -1.5041560657 6.8888729101 -0.1593400289
 N -1.9642525282 3.1254777376 -4.1857314293
 C -1.6611453106 6.5872448443 1.2275991667
 H -1.5068185473 7.5300288842 1.7539019813
 H -0.9273151456 5.8485238073 1.567076793
 H -2.6706273512 6.2113862575 1.4347826775
 C -3.6793226243 0.9697141967 2.5859579661
 C -4.9449236488 1.8491393927 2.4647249287
 H -3.6963650147 0.3234524431 3.465485023
 C -3.6142497111 0.7780873343 0.0548753124
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 C -5.7630638249 1.4022045313 1.238120237
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 C -0.7083184866 -4.0746020252 -1.7577509609

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 C -3.6963807024 -3.3414402238 -1.1965750176
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TS C-C RR

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.63862832 A.U.

B3LYP / 6-31+G(d,p)

SCF Done: E(RB3LYP) = -2990.82679472 A.U.

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 N -2.2656830575 0.994263309 0.3300785671
 N 0.96256159 0.7860689333 0.1695494741
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 C 2.9508007715 3.6212896621 0.6498783821
 C 2.8688766398 1.9408015998 2.3792424724
 C 2.8405523173 4.0972965029 -0.6881735741
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 C 3.1920383257 2.9407183276 3.3213303263
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TS C-C RS

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.63224568 A.U.

B3LYP / 6-31+G(d,p)

SCF Done: E(RB3LYP) = -2990.82175860 A.U.

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 H -6.0901163147 0.5463697631 -4.4012460015
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 C -6.2060189325 1.8363165184 0.2633546322
 C -4.1337756619 3.0258540267 0.5291801592
 C -6.9167729061 2.9883465452 0.593357147
 H -6.7504592073 0.9206487279 0.0525111018
 C -4.8447657732 4.1818760166 0.8676254871
 H -3.05118516 3.060160801 0.5324522011
 C -6.2375967982 4.1717952092 0.8962489373
 H -8.0027286284 2.957953935 0.6219398531
 H -4.2991201807 5.0897517052 1.1105482104

H -3.175442046 5.7620393489 0.36546219
 H -5.5743054867 6.1969322484 -0.1487764864
 C -4.2959703727 0.6564366178 1.6372065719
 C -3.6329998504 1.0719938182 2.8022170438
 C -5.5098123085 -0.0301780183 1.7754842505
 C -4.1507979539 0.7826494045 4.0650994566
 H -2.7100262604 1.6382335917 2.7297320437
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 H -6.0512028289 -0.3567581739 0.8947311838
 C -5.3540294491 0.0865888329 4.1903073608
 H -3.6126897447 1.109440268 4.9508316302
 H -6.9733873781 -0.8515849153 3.1177756815
 H -5.7591744427 -0.1381767885 5.1730815215
 H -0.2715170422 -5.4576237264 0.6685614404
 H -1.5433447163 -3.7762661535 -1.6318909097
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 C -1.2118765808 -3.4748492433 -4.365461407
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 H -0.2219562667 -2.1667646589 -2.9618324417
 H -0.9531385244 -2.8657159641 -5.2397599626
 H -1.2228593941 -4.5228750766 -4.686600262
 H -2.2306584624 -3.2047859774 -4.0625613243
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 H 0.2107320059 -6.0182082771 -1.390303017
 H 0.0968335352 -5.7623268241 -3.1118310412
 H -1.6482653836 -7.3710989074 -2.3195729604
 H -2.304265947 -6.1339957974 -1.225371785
 H -2.42324785 -5.9208692323 -2.9760980483

TS acylation *RR*

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.64057509 A.U.

B3LYP / 6-31+G(d,p)

SCF Done: E(RB3LYP) = -2990.82779430 A.U.

0 1

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 C -1.1833144276 1.5841222352 -0.6035636555
 C -1.1307811547 2.4072458388 -1.8533514151
 O -1.9169216216 3.0332075851 -2.5447844517
 O 1.3079579472 2.3646343651 -2.6487191569
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 N 1.0724739719 0.7389945151 0.164381169
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 H 0.6787038546 0.2269159118 0.9609195806
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 C 2.9994310424 1.9245175605 1.17022316
 C 3.5247573969 3.2138279009 0.8344567916
 C 2.9037541894 1.5905491772 2.5081802093
 C 3.6281302573 3.715057001 -0.4948815537
 C 3.9603535249 4.0417798929 1.9253879481
 C 3.348846023 2.4903652265 3.4995795252
 H 2.4796384395 0.6411498595 2.8227303864
 C 4.1494392281 4.9750630485 -0.727929825
 H 3.2449562526 3.1370427757 -1.3248880472
 C 4.50725259 5.3245461443 1.6395383636

H -6.7895889704 5.0702232671 1.1583043031
 C -4.4529880902 -0.4736183431 1.0166193433
 C -3.9913289986 -0.23841914 2.3225388899
 C -5.3209377461 -1.550393884 0.8032477054
 C -4.3607364549 -1.0739217124 3.3753379523
 H -3.3479145885 0.6128898278 2.5247769342
 C -5.7007823596 -2.3821540884 1.8609171514
 H -5.7036016154 -1.7509738655 -0.1906349643
 C -5.2186694022 -2.152983197 3.1486383035
 H -3.984157502 -0.8746220695 4.374949676
 H -6.3738006592 -3.2134505301 1.6690123774
 H -5.5108069064 -2.8032281204 3.9686108174
 H 0.0754591504 -5.4608398927 0.2295926012
 H 0.858315908 -3.6040671423 -1.5567478058
 H 3.2173390832 -4.1760851902 -1.6604345139
 C 3.6203811217 -4.616565249 0.395438289
 C 5.0582449423 -5.0192040885 0.0437248864
 H 3.2348069299 -5.2944193134 1.1660545342
 H 3.6174421415 -3.6144792925 0.8375917348
 H 5.69575822 -5.014391225 0.9357948616
 H 5.1106117745 -6.02502388 -0.3894907932
 H 5.5005436077 -4.3247074658 -0.682201938
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 H 1.7678705351 -6.5493952211 -0.4147592132
 H 3.1693280783 -6.5857650363 -1.4547316101
 H 1.2203327472 -7.1428877712 -2.8070236843
 H 0.3534238354 -5.6855050916 -2.312717642
 H 1.7921852532 -5.5540001965 -3.3351379766

TS acylation *RS*

B3LYP / 6-31G(d)

SCF Done: E(RB3LYP) = -2990.63597211 A.U.

B3LYP / 6-31+G(d,p)

SCF Done: E(RB3LYP) = -2990.82549765 A.U.

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 C 2.3785632683 1.7755921764 1.7629494991
 O 3.4079398852 2.1405035716 2.2996915855
 O 0.2361456393 3.0310366818 2.3885501531
 N 2.5880100687 -0.2445532648 0.0754209404
 N -0.4441492731 0.9807193279 -0.0206447789
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 H -0.4006244084 0.2821875688 -0.77218523
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 C -1.1452175995 2.9037419617 -1.4405214574
 C -0.8300328809 4.2989796787 -1.3574530434
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 C -0.4170120645 6.375822537 -0.1503911122
 H -0.824884963 4.5149046887 0.8089787872
 C -0.309873603 6.3826803749 -2.5662124126

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 C 0.3275242149 -3.0806386421 2.1313882456
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 C 4.0151525397 -0.6626697218 0.1891418435
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 C 5.4388477982 -0.3210486743 2.3354801677

C -4.2794204408	0.856428196	-2.1171140462	C 3.4984172724	-1.7446493373	2.4226432791
C -4.39555664	-0.9010342766	-0.4750364838	C 5.6887022696	-0.5837046667	3.6857360694
C -4.7344672096	-0.0313474584	-3.0953613188	H 6.095899127	0.3552399874	1.8030980013
H -4.0180181252	1.869813406	-2.3988818712	C 3.7451199924	-2.0031302487	3.7702699473
C -4.8440946617	-1.7899358443	-1.4526544652	H 2.6471718879	-2.2111321395	1.9359775257
H -4.242803382	-1.2684926864	0.5330475862	C 4.8451372362	-1.4248028015	4.4092797993
C -5.0305686041	-1.3552779262	-2.7665824523	H 6.5420373869	-0.1164694622	4.170151731
H -4.8539809641	0.3178652094	-4.1177524867	H 3.0764469068	-2.6603935266	4.3202716225
H -5.0366427453	-2.8229953825	-1.1787523108	H 5.0383744351	-1.6255621358	5.4597899438
H -5.3914791576	-2.0428627383	-3.527072514	C 4.9513202453	0.3711232415	-0.4895932511
C -3.8861310648	2.8842042308	0.091540445	C 6.3044310049	0.0403113403	-0.6794891071
C -5.1367263219	3.2776132128	-0.4060956763	C 4.5031826744	1.6059951292	-0.9693551792
C -3.0108279495	3.8818593602	0.5421729254	C 7.1828239004	0.9249628889	-1.3016919183
C -5.4866234316	4.62635559989	-0.4831938142	H 6.6731659488	-0.9243502317	-0.3440207522
H -5.8468018835	2.5302990736	-0.7429700233	C 5.3816752361	2.4931921191	-1.600293822
C -3.3580287805	5.2311994657	0.4630543309	H 3.4626964994	1.8891763422	-0.8723456837
H -2.0498916732	3.6081975301	0.9640727867	C 6.7245984319	2.161238805	-1.765265065
C -4.5965888603	5.6120131879	-0.0544365381	H 8.2242843209	0.6432037839	-1.4318575703
H -6.4592959145	4.903244399	-0.8811495052	H 5.0049526504	3.4454038729	-1.9639471556
H -2.6559887209	5.9842759203	0.8111568427	H 7.4059547931	2.851170567	-2.2554231271
H -4.8670696841	6.6624517171	-0.1177564	C 4.1298383271	-1.96737927	-0.6460550948
C -4.0812197998	1.0589375456	1.7140243355	C 3.6326082905	-1.9764374158	-1.9603474059
C -3.2630063764	1.1332074216	2.8489615076	C 4.7688294754	-3.1168915219	-0.1693905849
C -5.4463351531	0.7891250143	1.8998392879	C 3.7411686851	-3.1126555377	-2.7602845879
C -3.7875964485	0.9196973506	4.1268444137	H 3.1706307041	-1.0827937637	-2.3713508923
H -2.2087076283	1.3652789028	2.7520052714	C 4.89004018	-4.2524369726	-0.976060004
C -5.9709963766	0.5794770396	3.1738832839	H 5.171140188	-3.1360318122	0.8367050934
H -6.107773981	0.7358689532	1.0414518006	C 4.3707276041	-4.2593148837	-2.2696246853
C -5.1422227182	0.6397231622	4.2968344891	H 3.3416044765	-3.0972901324	-3.7706222882
H -3.128201117	0.9766575442	4.9887558514	H 5.3887908365	-5.1341558515	-0.5827854269
H -7.030654615	0.3667700443	3.2869943897	H 4.4600660109	-5.1448800738	-2.8927307682
H -5.5497679565	0.4733817674	5.2901779517	H -1.105498043	-4.9854925029	0.9027113903
H -0.9644956026	-5.4026444186	0.041089247	H -1.6697463157	-2.7240763488	1.8814858846
H -1.9702594833	-3.1016115661	-1.7968583915	H -4.0053541028	-2.8051438935	2.0308140739
C -0.3830599802	-2.5253181891	-3.1061754544	C -4.546546815	-3.9266804494	0.2873623032
C -1.2898025538	-2.2518106414	-4.3116965174	C -6.0220121085	-3.9223312273	0.7091138391
H 0.5796357663	-2.9284783853	-3.4590384676	H -4.3061159176	-4.898780572	-0.1598316566
H -0.1678971675	-1.5784776783	-2.6006787215	H -4.3917269053	-3.1784150865	-0.4966939499
H -0.8108625296	-1.5527540882	-5.0074337913	H -6.6732492701	-4.1261218741	-0.1490293044
H -1.520780906	-3.1654960814	-4.8723081817	H -6.2384093697	-4.6813935149	1.4699282122
H -2.2393589853	-1.8066072469	-3.9929041688	H -6.3174355387	-2.9493201933	1.1228414493
C -1.1498824014	-4.9304033376	-2.6545301476	C -3.4165891633	-4.8250035035	2.3964517598
C -2.5795830558	-5.4828155556	-2.588031649	C -2.5776365515	-4.5740059216	3.6571529539
H -0.4696884191	-5.6235534257	-2.1389570752	H -3.0074325046	-5.6856058941	1.8488784404
H -0.8199779381	-4.9376226479	-3.7008786639	H -4.4226545877	-5.1321019329	2.7092724138
H -2.9520373101	-5.5106537268	-1.5584049719	H -2.6283967495	-5.4365807546	4.3315134141
H -3.2666548637	-4.8529054477	-3.166125966	H -1.5202967704	-4.4006225327	3.4291849365
H -2.6315395291	-6.4982780957	-2.9991057349	H -2.9447308652	-3.6997942953	4.2098950203

In order to rationalize the stereochemical outcome of this project a DFT study on the reaction between homophthalic anhydride **1** and 2-ethylbutanal (**53**) have been carried out. For this particular case only the two major enantiomers have been taken into account, *cis*-(*R,R*) and *trans*-(*R,S*). By analogy with observations made in the catalytic cycloaddition reaction between homophthalic anhydride and benzaldehyde¹⁴ we assumed that the reaction proceeds *via* ‘specific-like catalysis’. The enolate, generated from deprotonation by the quinuclidine moiety, interacts with the squaramide moiety *via* a double hydrogen bonding interaction, while the aldehyde is activated by the protonated quinuclidine unit (Binding mode A - Figure S2).

Our experimental data indicated that the two major stereoisomers yielded were (*R,S*)-35 and (*R,R*)-35. Thus, based on the binding mode previously mentioned, we proposed two different pre-TS assemblies for both diastereomers (Figure S1) and studied their relative energy profiles (Figure S2). The computational analysis showed that the pathway leading to (*R,S*)-35 is favored as the barriers associated with the formation of (*R,R*)-35 are higher than those related to the formation of the more stable (*R,S*)-35 (Figure S2). Albeit it is noteworthy that when starting at the catalyst-bound adduct, the barrier to its collapse to starting materials is lower than the barrier to lactonisation.

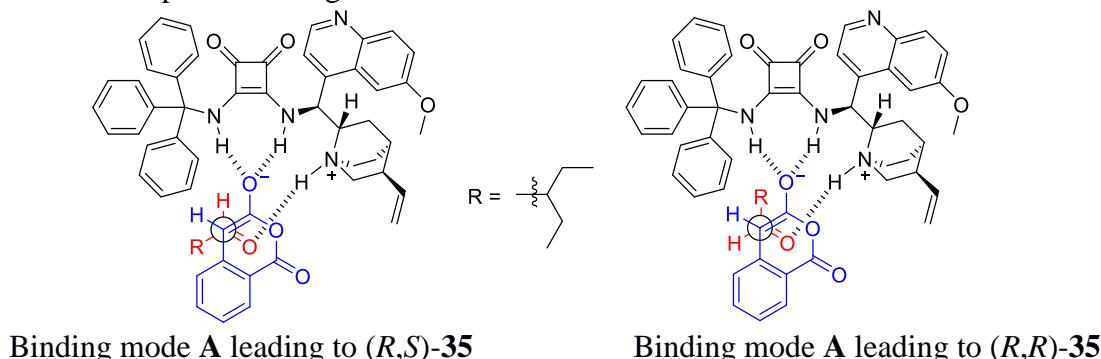


Figure S2 Pre-TS assemblies leading to (*R,S*)-35 and (*R,R*)-35 according to binding mode A.

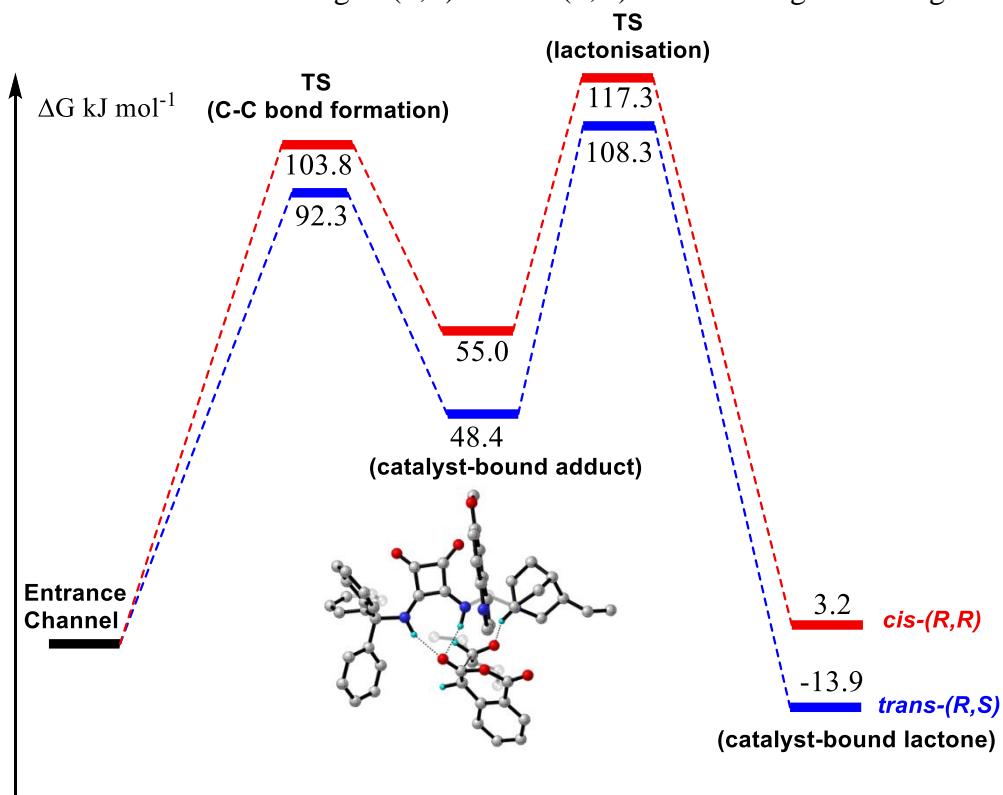


Figure S3 Potential energy surfaces for (*R,S*)-35 and (*R,R*)-35 complexes formed via binding mode A at B3LYP/ computational lev6-31+g(d) level in PCM-THF.

As this model was unable to explain the stereoinduction observed experimentally we investigated a second possible binding mode (**B**), in which two oxygen atoms of the anhydride are orientated towards the trityl group of the catalyst (Figure S3). In this case, higher energetic barriers were observed to the formation of the 1,2-adducts. However, the significantly lower energy of the *cis*-adduct (40.4 kJ mol^{-1}) relative to that of the *trans*-adduct (*R,S*) (76.3 kJ mol^{-1}), in addition to very similar barriers to its subsequent lactonisation or reversion to starting materials and a more stable *cis*-product, could potentially explain the origins of the observed sense of stereoinduction (Figure

S4). The calculated dr (93:7) was in excellent agreement with experimental data dr (90:10). Besides the ratio of cis and trans products predicted from the four pathways together using the Boltzmann distribution has been calculated. Obtaining a theoretical dr (88:12), it is slightly lower than the experimental result, but it still shows the cis product is favoured.

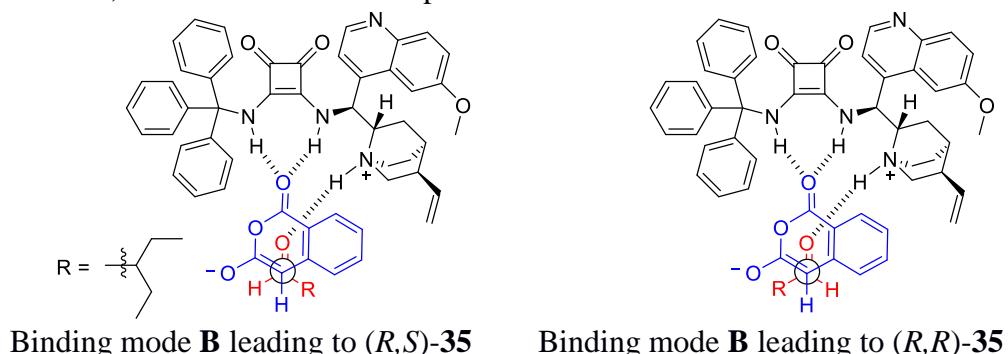


Figure S4 Pre-TS assemblies leading to (R,S) -35 and (R,R) -35 according to binding mode B.

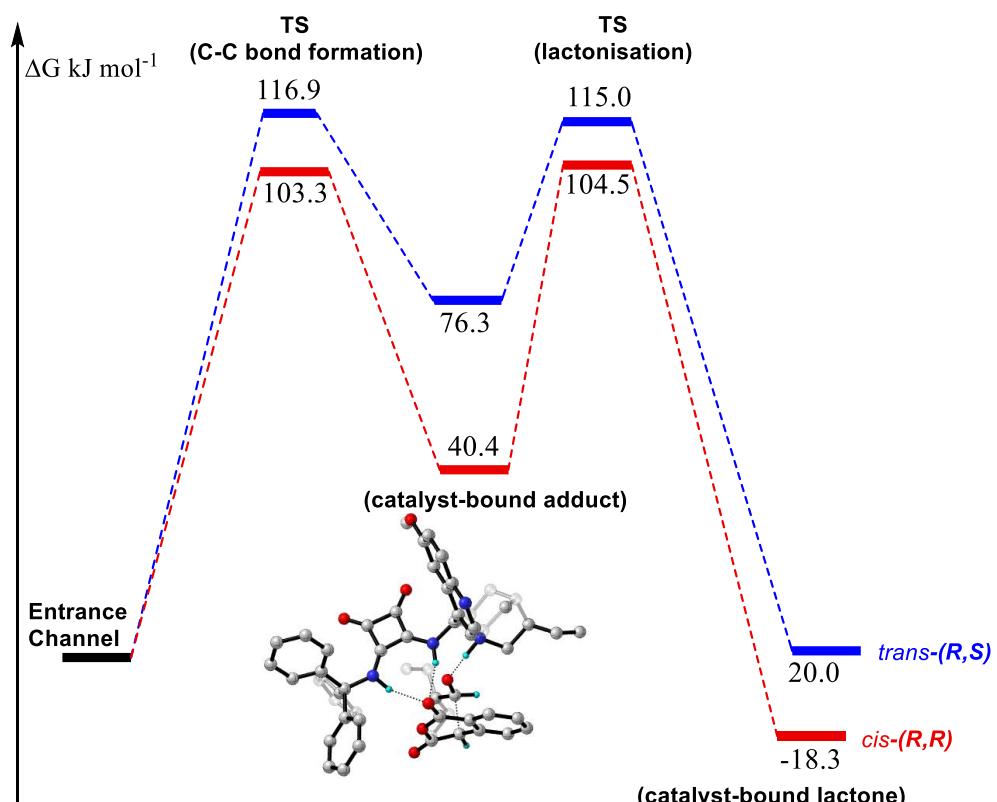


Figure S5 Potential energy surfaces for (R,S) -35 and (R,R) -35 complexes formed via binding mode B at B3LYP/ computational lev6-31+g(d) level in PCM-THF.

In further support of this hypothesis, QTAIM (quantum theory of atoms in molecules) revealed that the stereochemical outcome is also governed by a web of attractive interactions involving hydrogen atoms on the trityl phenyl rings of the catalyst and the two oxygen atoms of the anhydride, which influence the facial selectivity of the attack of the anhydride enolate to the aldehyde (Figure S5). This also provides an explanation for the profound influence of the trityl unit on diastereoccontrol,

which is not mimicked by any other squaramide substituent evaluated.

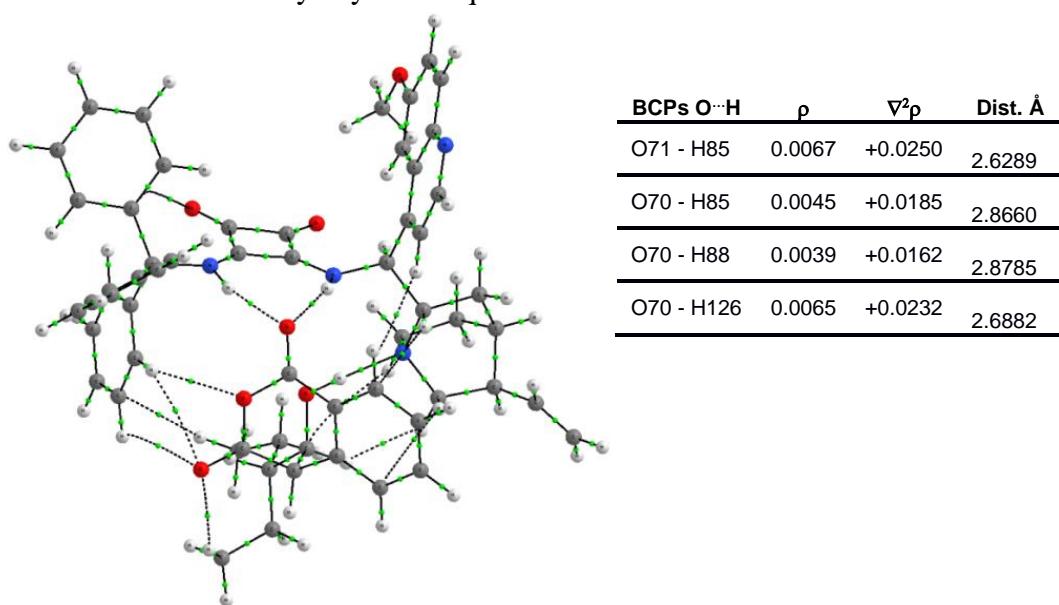


Figure S6 QTAIM interactions contributing to the formation of (*R,R*)-**35** corresponding to binding mode **B**. Electron density [ρ (BCP), a.u.] and Laplacian [$\nabla^2\rho$ (BCP), a.u.] calculated at B3LYP/6-31G(d) in PCM-THF computational level, using the QTAIM theory.

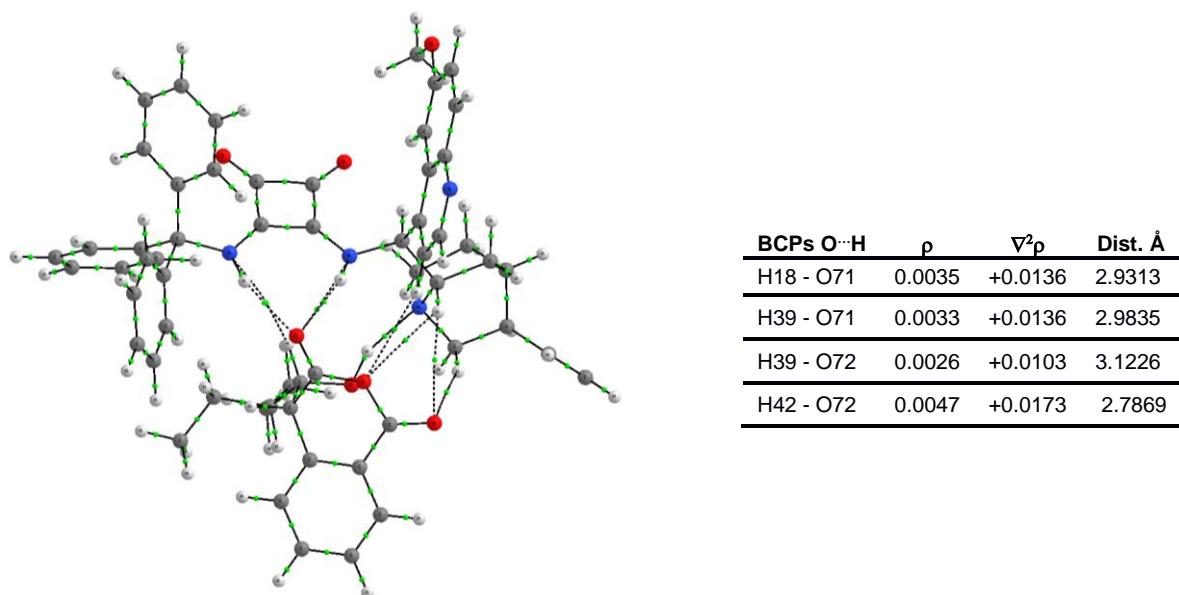


Figure S7 QTAIM interactions contributing to the formation of (*R,S*)-**35** corresponding to binding mode **A**. Electron density [ρ (BCP), a.u.] and Laplacian [$\nabla^2\rho$ (BCP), a.u.] calculated at B3LYP/6-31G(d) in PCM-THF computational level, using the QTAIM theory.

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