Supporting Information

Enantioselective Aminocatalytic [2+2] Cycloaddition through Visible Light Excitation

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1. General Information

The ^{1}H and ^{13}C NMR spectra were recorded on a *Bruker Avance 300 MHz or 500 MHz spectrometer* at 300 or 500 MHz for ^{1}H and at 75 or 126 MHz for ^{13}C, respectively. The ^{19}F spectra were recorded on a *Bruker Avance 300 MHz spectrometer* at 282 MHz. The chemical shifts (δ) for ^{1}H NMR are reported relative to the tetramethylsilane signal at 0 ppm or relative to the residual signal of the solvent ($CDCl_3$ at 7.26 ppm), while for ^{13}C NMR are given in ppm relative to the residual signal of the solvent ($CDCl_3$ at 77.16 ppm). Coupling constants are given in Hz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; sxt, sextet; hept, heptet; m, multiplet; br, broad signal.

Optical rotations were recorded on a *Perkin Elmer 241 MC* Polarimeter in a 10 cm path length cell in HPLC grade $CHCl_3$ (concentration in g/100 mL).

Enantiomeric ratios were determined by Supercritical Fluid Chromatography (SFC) on chiral columns on an *Agilent Technologies 1260 Infinity Series* instrument, employing *Daicel Chiralpak* IA, IB-3, IC, ID-3 and IG-3 columns and a UV-Vis detector. The exact conditions for the analyses are specified in each case.

High-Resolution Mass Spectra (HRMS) were obtained on an *Agilent Technologies 6120 Quadrupole LC/MS* coupled with an SFC *Agilent Technologies 1260 Infinity Series* instrument for the ESI-MS (Electrospray Ionization) or on an *Agilent Technologies 5977B MSD* coupled with an *Agilent Technologies 7820A GC System* for the EI-MS (Electron Ionization mass spectroscopy). *MassWorks* software version 4.0.0.0 (*Cerno Bioscience*) was used for the formula identification. *MassWorks* is an MS calibration software which calibrates isotope profiles to achieve high mass accuracy and enables elemental composition determination on conventional mass spectrometers of unit mass resolution allowing highly accurate comparisons between calibrated and theoretical spectra.[1]

UV-Vis measurements were carried out on an *Agilent 8453 UV-Visible Spectroscopy System* controlled by *UV-Visible ChemStation Software*. MTBE and a Teflon-top 10x10 mm precision cell made of Quartz SUPRASIL® were used for all absorption measurements. The solution concentration used for recording the absorption spectra was 0.05 M (0.1 mmol of **1a**, 0.02 mmol of catalyst **3**, 0.1 mmol of TFA, and 2 mL of solvent).

Crystals of compound **5a** were mounted at low temperature in inert oil on a glass fiber. Data were collected on a *Bruker X8 APPEX II* CCD-based diffractometer, equipped with a graphite monochromated MoKα (radiation source λ = 0.71073 Å). Data were integrated using *SAINT*[2] and an absorption correction was performed with the program *SADABS*.[3] The structures were solved by direct methods using *SHELXTL*,[4] and refined by fullmatrix least-squares methods based on F^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. All H atoms were computed and refined with an overall isotropic temperature factor using a riding model.

2. Materials and Methods

Commercial grade reagents and solvents were purchased from *Sigma-Aldrich, Alfa Aesar, Fluorochem, Acros Organics, TCI Chemicals, Strem Chemicals* and used without further purifications while anhydrous solvents were taken from a SPS solvent dispenser. Chromatographic purification of products was accomplished using flash chromatography (FC) on *Merck* Geduran® Si 60 silica gel (40-63 μm). Thin layer chromatography (TLC) was performed on *Merck* precoated TLC plates (silica gel 60 F254).

3. Photoreactor Setup

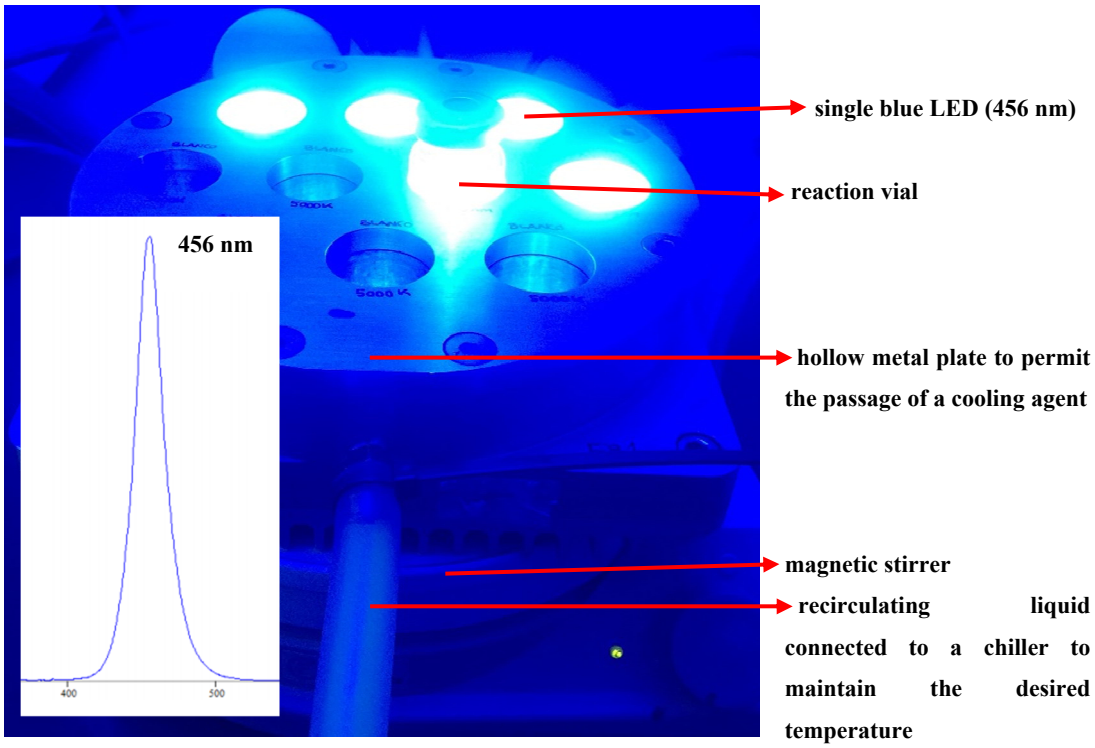
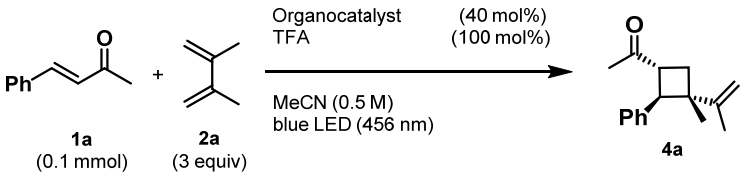
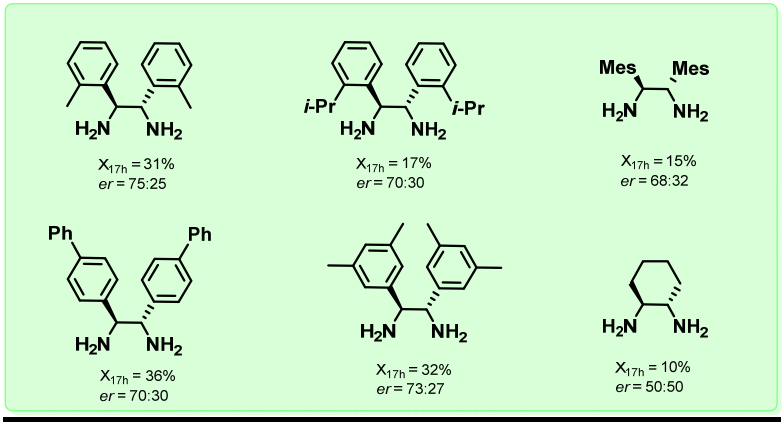


Figure S1: Photoreactor setup.

4. Optimization Studies

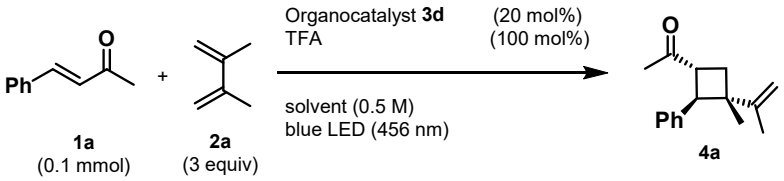
Table S1: Catalyst screening (selected examples)





Conversion determined by ^{1}H NMR of the crude mixture after 17h. *er* determined by chiral SFC analysis of the isolated product.

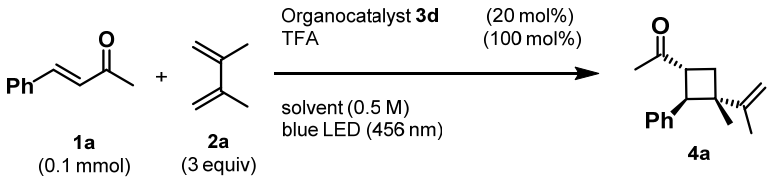
Table S2: Solvent screening (selected examples)



Solvent	Conversion[a](%)	er[b]
$CHCl_3$	100	76:24
Toluene	100	82:18
DMF	17	42:58
i-PrOAc	71	85:15
n-Hexane	90	70:30
p-Xylene	100	81:19
THF	55	82:18
Acetone	17	65:35
MTBE	100	88:12
Et_2O	**100**	**90:10**

[a] Determined by ^{1}H NMR of the crude mixture after 17h. [b] Determined by chiral SFC analysis of the isolated product.

Table S3: Reaction conditions screening (selected examples)

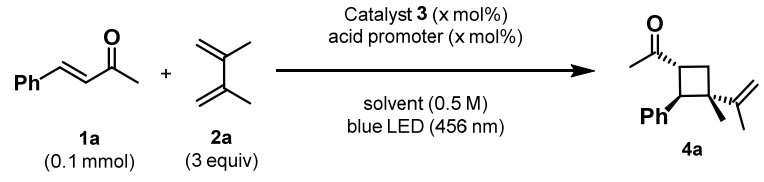


1a (0.1 mmol) + 2a (3 equiv) → 4a

Solvent	Reaction Deviation	Conversion[a](%)	Isolated Yield(%)	er[b]
MTBE	**none**	100	83%	88:12
MTBE	**T = 278 K**	100[c]	88%	80:20
MTBE	**1.5 equiv of 2a**	82	66%	87:13
MTBE	**6 equiv of 2a**	100	74%	88:12
MTBE	**TFA (50 mol%)**	87	69%	86:14
diethyl ether	**3d (10 mol%)**	100[c]	93%	88:12
diethyl ether	**under air**	100	74%	82:18

[a] Determined by ^{1}H NMR of the crude mixture after 17h. [b] Determined by chiral SFC analysis of the isolated product. [c] Determined by ^{1}H NMR of the crude mixture after 40h

Table S4: Acid promoter screening (selected examples)



1a (0.1 mmol) + 2a (3 equiv) → 4a

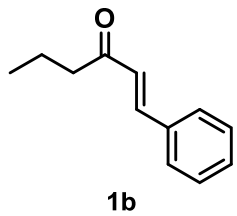
Solvent	Catalyst (mol%)	Acid Promoter (mol%)	Conversion[a](%)	er[b]
MTBE	**3d (20)**	**TFA (100)**	**100**	**88:12**
MTBE	**3d (20)**	**TFA (50)**	**87**	**86:14**
MTBE	**3d (20)**	**TFA (25)**	**59**	**85:15**
MTBE	**3a (20)**	**TFA (100)**	**37**	**77:23**
MTBE	**3a (20)**	**(*L*)-Malic acid (100)**	**7**	**50:50**
MTBE	**3a (20)**	**(*S*)-Camphorsulfonic acid (100)**	**0**	**.**
MTBE	**3a (20)**	**(*D*)-Tartaric acid (100)**	**0**	**.**
MTBE	**3a (20)**	**(*R*)-Mandelic acid (100)**	**11**	**50:50**
MTBE	**3a (20)**	**(*R*)-Mosher's acid (100)**	**18**	**55:45**
MeCN	**3a (40)**	**TFA (100)**	**27**	**73:27**
MeCN	**3a (40)**	**TCA (100)**	**19**	**71:29**
MeCN	**3a (40)**	***p*-TsOH (100)**	**0**	**-**
MeCN	**3a (40)**	**TfOH (100)**	**11**[c]	**-**
MeCN	**3a (40)**	**2,6-dinitrobenzoic acid (100)**	**12**	**65:35**
MeCN	**3a**[d] **(40)**	**-**	**11**	**52:48**

[a] Determined by ^{1}H NMR of the crude mixture after 17h. [b] Determined by chiral SFC analysis of the isolated product. [c] complex mixture and visible degradation [d] As 2·HCl salt

5. Experimental Procedures and Characterization

5.1 Characterization data for the ketones (1b-l)

(*E*)-1-Phenylhex-1-en-3-one (1b)



1b

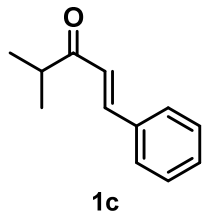
To a stirred solution of 2-pentanone (5 mmol) in methanol (5mL) 25 mL of 1 M NaOH solution were added. Then, benzaldehyde (5.5 mmol, 1.1 equiv.) was added dropwise and stirring maintained overnight. 25 mL of diethyl ether were added and the organic phase separated. The aqueous phase was extracted with diethyl ether, thus, the reunited organic phases were washed with brine and dried over magnesium sulfate. After flash chromatography (CyHex : EtOAc = 95 : 5) and removal of the solvents under reduced pressure 592 mg of **1b** were obtained as a colorless oil (68% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 – 7.50 (m, 3H), 7.42 – 7.37 (m, 3H), 6.74 (d, *J* = 16.2 Hz, 1H), 2.65 (t, *J* = 7.3 Hz, 2H), 1.72 (sxt, *J* = 7.3 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 199.9, 141.9, 134.4, 130.1, 128.6, 128.0, 126.0, 42.5, 17.5, 13.6.

HRMS (ESI): calculated for $C_{12}H_{15}O^+$, $[M+H]^+$ = 175.1117; found = 175.1110.

(*E*)-4-Methyl-1-phenylpent-1-en-3-one (1c)



1c

To a stirred solution of 3-methyl-2-butanone (5 mmol) in methanol (5mL) 25 mL of 1 M NaOH solution were added. Then, benzaldehyde (5.5 mmol, 1.1 equiv.) was added dropwise and stirring maintained overnight. 25 mL of diethyl ether were added and the organic phase separated. The aqueous phase was extracted with diethyl ether, thus, the reunited organic phases were washed with brine and dried over magnesium sulfate. After flash chromatography (CyHex : EtOAc = 95 : 5) and removal of the solvents under reduced pressure 636 mg of **1c** were obtained as a white solid (73% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61 (d, *J* = 16.1 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.44 – 7.35 (m, 3H), 6.82 (d, *J* = 16.0 Hz, 1H), 2.94 (hept, *J* = 6.9 Hz, 1H), 1.19 (d, *J* = 6.9 Hz, 6H).

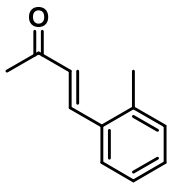
^{13}C NMR (75 MHz, $CDCl_3$): δ 203.6, 142.3, 134.7, 130.3, 128.8, 128.2, 124.4, 39.2, 18.4.

HRMS (ESI): calculated for $C_{12}H_{15}O^+$, $[M+H]^+$ = 175.1117; found = 175.1113.

General procedure for the synthesis of α,β-unsaturated ketones (1d-l)

To a stirred 1 M NaOH solution (25 mL) acetone (100 mmol) was added followed by dropwise addition of a solution of the appropriate aldehyde (5 mmol) in methanol (5 mL). The reaction mixture was stirred overnight at room temperature. 25 mL of diethyl ether were added and the organic phase separated. The aqueous phase was extracted with diethyl ether, the reunited organic phases were washed with brine and dried over magnesium sulfate. After flash chromatography the corresponding ketone **1** was obtained as a pure product.

(*E*)-4-(o-Tolyl)but-3-en-2-one (1d)



1d

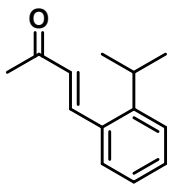
1d was prepared according to the general procedure employing 2-methylbenzaldehyde and purified by flash chromatography (CyHex : EtOAc = 90 : 10) to obtain 500 mg of **1d** as a colorless oil (62% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, *J* = 16.1 Hz, 1H), 7.60 – 7.55 (m, 1H), 7.35 – 7.19 (m, 3H), 6.66 (d, *J* = 16.1 Hz, 1H), 2.46 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 140.2, 137.4, 133.0, 130.5, 129.8, 127.6, 126.1, 126.0, 27.3, 19.3.

HRMS (ESI): calculated for $C_{11}H_{13}O^+$, $[M+H]^+$ = 161.0961; found = 161.0979.

(*E*)-4-(2-isopropylphenyl)but-3-en-2-one (1e)



1e

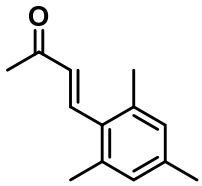
1e was prepared according to the general procedure employing 2-isopropylbenzaldehyde and purified by flash chromatography (CyHex : EtOAc = 90 : 10) to obtain 715 mg of **1e** as a colorless oil (76% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (d, *J* = 15.9 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.39 – 7.29 (m, 2H), 7.23 – 7.16 (m, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 3.33 (hept, *J* = 6.9 Hz, 1H), 2.37 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 198.2, 148.1, 140.9, 132.4, 130.4, 128.7, 126.8, 126.1, 125.5, 29.3, 27.9, 23.6.

HRMS (ESI): calculated for $C_{13}H_{17}O^+$, $[M+H]^+$ = 189.1274; found = 189.1255.

(*E*)-4-mesitylbut-3-en-2-one (1f)



1f

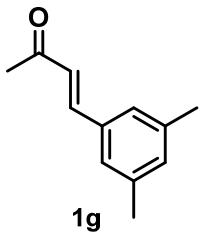
1f was prepared according to the general procedure employing 2,4,6-trimethylbenzaldehyde and purified by flash chromatography (CyHex : EtOAc = 90 : 10) to obtain 800 mg of **1f** as a white solid (85% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (d, *J* = 16.6 Hz, 1H), 6.89 (s, 2H), 6.33 (d, *J* = 16.6 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 6H), 2.28 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 198.5, 142.0, 138.6, 136.8, 132.5, 131.0, 129.3, 27.5, 21.1.

HRMS (ESI): calculated for $C_{13}H_{17}O^+$, $[M+H]^+$ = 189.1274; found = 189.1301.

(*E*)-4-(3,5-dimethylphenyl)but-3-en-2-one (1g)



1g

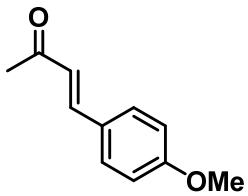
1g was prepared according to the general procedure employing 3,5-dimethylbenzaldehyde and purified by flash chromatography (CyHex : EtOAc = 90 : 10) to obtain 688 mg of **1g** as a colorless oil (79% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (d, *J* = 16.3 Hz, 1H), 7.12 (s, 2H), 6.99 (s, 1H), 6.66 (d, *J* = 16.3 Hz, 1H), 2.32 (s, 3H), 2.29 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 198.0, 143.6, 138.3, 134.2, 132.2, 126.6, 126.0, 27.2, 21.0.

HRMS (ESI): calculated for $C_{12}H_{15}O^+$, $[M+H]^+$ = 175.1117; found = 175.1137.

(*E*)-4-(4-Methoxyphenyl)but-3-en-2-one (1h)



1h

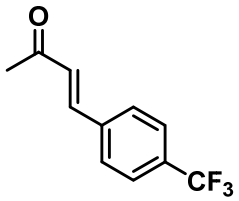
1h was prepared according to the general procedure employing 4-methoxybenzaldehyde and purified by flash chromatography (CyHex : EtOAc = 90 : 10) to obtain 485 mg of **1h** as a white solid (55% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 – 7.40 (m, 3H), 6.92 – 6.85 (m, 2H), 6.57 (d, *J* = 16.2 Hz, 1H), 3.81 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 161.2, 142.7, 129.6, 126.6, 124.5, 114.0, 54.9, 26.9.

HRMS (ESI): calculated for $C_{11}H_{13}O_2^+$, $[M+H]^+$ = 177.0910; found = 177.0914.

(*E*)-4-(4-(Trifluoromethyl)phenyl)but-3-en-2-one (1i)



1i

1i was prepared according to the general procedure employing 4-(trifluoromethyl)benzaldehyde and purified by flash chromatography (CyHex : EtOAc = 90 : 10) to obtain 643 mg of **1i** as a white solid (60% yield).

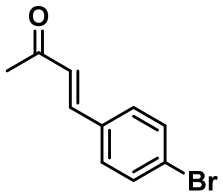
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (s, 4H), 7.46 (d, *J* = 16.3 Hz, 1H), 6.71 (d, *J* = 16.4 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 141.0, 137.9, 132.2, 131.8, 131.3, 130.9, 129.0, 128.2 (2C), 125.73, 125.68, 125.63, 125.58, 27.4.

^{19}F NMR (282 MHz, $CDCl_3$): δ -62.99.

HRMS (ESI): calculated for $C_{11}H_{10}F_3O^+$, $[M+H]^+$ = 215.0678; found = 215.0692.

(*E*)-4-(4-Bromophenyl)but-3-en-2-one (1j)



1j

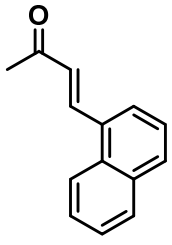
1j was prepared according to the general procedure employing 4-bromobenzaldehyde and purified by flash chromatography (CyHex : EtOAc = 90 : 10) to obtain 504 mg of **1j** as a white solid (45% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 – 7.47 (m, 2H), 7.46 – 7.35 (m, 3H), 6.68 (d, *J* = 16.3 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 141.5, 133.1, 131.9, 129.4, 127.3, 124.4, 27.4.

HRMS (ESI): calculated for $C_{10}H_{10}BrO^+$, $[M+H]^+$ = 224.9910; found = 224.9935.

(*E*)-4-(Naphthalen-1-yl)but-3-en-2-one (1k)



1k

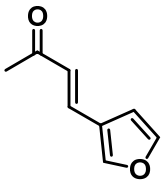
1k was prepared according to the general procedure employing 1-naphthaldehyde and purified by flash chromatography (CyHex : EtOAc = 90 : 10) to obtain 687 mg of **1k** as a yellow oil (70% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (d, *J* = 16.0 Hz, 1H), 8.22 – 8.15 (m, 1H), 7.96 – 7.87 (m, 2H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.63 – 7.46 (m, 3H), 6.83 (d, *J* = 16.0 Hz, 1H), 2.48 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 197.4, 139.2, 133.2, 131.0, 130.9, 130.2, 128.8, 128.3, 126.4, 125.7, 124.9, 124.5, 122.6, 27.3.

HRMS (ESI): calculated for $C_{14}H_{13}O^+$, $[M+H]^+$ = 197.0961; found = 197.0965.

(*E*)-4-(Furan-3-yl)but-3-en-2-one (1l)



1l

1l was prepared according to the general procedure employing 3-furancarboxaldehyde and purified by flash chromatography (CyHex : EtOAc = 90 : 10) to obtain 301 mg of **1l** as an orange solid (44% yield).

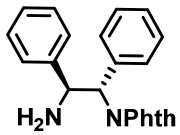
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62 (br s, 1H), 7.41 – 7.29 (m, 2H), 6.53 (br s, 1H), 6.36 (br d, *J* = 16.2 Hz, 1H), 2.24 (br s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 198.0, 144.9, 144.5, 133.3, 127.1, 122.7, 107.3, 27.1.

HRMS (ESI): calculated for $C_8H_9O_2^+$, $[M+H]^+$ = 137.0597; found = 137.0615.

5.2 Synthesis of the diamine catalysts (3b-c)

2-((1*S*,2*S*)-2-Amino-1,2-diphenylethyl)isoindoline-1,3-dione (S1)[5]

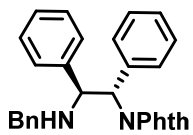


S1

In a 20 mL round-bottom flask 951 mg (5.0 mmol) of *para*-toluensulfonic acid monohydrate were weighted and 5 mL of anhydrous toluene were added. Thus, the solvent was removed under reduced pressure to azeotropically remove the water (3x). Then, 5 mmol of commercially available **3a** and 5 mmol of phthalic anhydride were added. After the addition of 5 mL of anhydrous toluene the reacton mixture was stirred at reflux for 62 hours obtaining a white precipitate. 5 mL of *n*-Hexane were added and the solid was filtered over a Büchner funnel washing several times with *n*-Hexane. The collected solid was dissolved in 30 mL of DCM and stirred for 5 hours with 30 mL of a saturated solution of potassium carbonate. The aqueous phase was separated, the organic layer was washed with brine and dried over magnesium sulfate. After removal of the solvents under reduced pressure the residue was purified by flash chromatography (CyHex : EtOAc = gradient from 1 : 1 to 0 : 1) obtaining 1185 mg of **S1** as a white solid (69% yield).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.87 – 7.81 (m, 2H), 7.73 – 7.66 (m, 2H), 7.45 – 7.37 (m, 2H), 7.31 – 7.11 (m, 8H), 5.43 (d, *J* = 10.9 Hz, 1H), 5.33 (d, *J* = 11.0 Hz, 1H), 1.69 (br s, 2H).

2-((1*S*,2*S*)-2-(Benzylamino)-1,2-diphenylethyl)isoindoline-1,3-dione (S2)



S2

In a 20 mL round-bottom flask, 342.4 mg (1.0 mmol) of **S1** and 318 mg (2.3 mmol) of potassium carbonate were weighted. Thus, 5 mL of acetonitrile were added, followed by dropwise addition of benzyl bromide (2.5 mmol). The reaction mixture was stirred at reflux for 15 hours. The solvents were removed under reduced pressure, the residue was suspended in $CHCl_3$, washed with a saturated solution of sodium bicarbonate and dried over magnesium sulfate. After purification by flash chromatography 263.7 mg of **S2** were obtained as a white solid (61% yield).

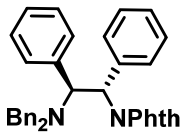
$[\alpha]^{20}_D$ = - 12.5 (*c* = 1.055, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 – 7.69 (m, 2H), 7.56 – 7.50 (m, 2H), 7.46 – 7.41 (m, 2H), 7.30 – 7.25 (m, 2H), 7.22 – 7.03 (m, 11H), 5.52 (d, *J* = 11.2 Hz, 1H), 5.09 (d, *J* = 11.2 Hz, 1H), 3.63 – 3.50 (m, 2H), 1.76 (br s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.7, 140.8, 140.3, 137.6, 133.8, 131.9, 129.4, 128.4, 128.2, 128.1, 128.05, 128.02, 127.7, 127.4, 126.7, 123.1, 61.8, 61.2, 51.1.

HRMS (ESI): calculated for $C_{29}H_{25}N_2O_2^+$, $[M+H]^+$ = 433.1911; found = 433.1919.

2-((1*S*,2*S*)-2-(Dibenzylamino)-1,2-diphenylethyl)isoindoline-1,3-dione (S3)



S3

In a 20 mL round-bottom flask, 342.4 mg (1.0 mmol) of **S1** and 318 mg (2.3 mmol) of potassium carbonate were weighted. Thus, 5 mL of acetonitrile were added, followed by dropwise addition of benzyl bromide (2.5 mmol). The reaction mixture was stirred at reflux for 15 hours. The solvents were removed under reduced pressure, the residue was suspended in $CHCl_3$, washed with a saturated solution of sodium bicarbonate and dried over magnesium sulfate. After purification by flash chromatography 86.4 mg of **S3** were obtained as a white solid (17% yield).

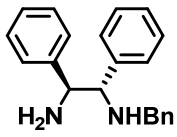
$[\alpha]^{20}_D$ = + 192 (*c* = 0.54, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 – 7.79 (m, 1H), 7.69 (dt, *J* = 5.6, 3.3 Hz, 3H), 7.39 (d, *J* = 7.1 Hz, 2H), 7.28 (d, *J* = 4.1 Hz, 4H), 7.23 – 7.09 (m, 11H), 7.08 – 6.96 (m, 3H), 6.15 (d, *J* = 12.0 Hz, 1H), 5.27 (d, *J* = 12.0 Hz, 1H), 3.95 (d, *J* = 13.3 Hz, 2H), 3.04 (d, *J* = 13.4 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 168.5, 167.2, 139.3, 136.8, 134.2, 133.9, 133.8, 132.6, 131.9, 130.3, 130.1, 129.2, 128.2, 128.0 (2C), 127.6, 127.4, 126.9, 123.3, 123.2, 61.4, 54.7, 54.2.

HRMS (ESI): calculated for $C_{36}H_{31}N_2O_2^+$, $[M+H]^+$ = 523.2380; found = 523.2365.

(1*S*,2*S*)-*N*1-Benzyl-1,2-diphenylethane-1,2-diamine (3b)



3b

263.7 mg (0.610 mmol) of **S2** were dissolved in 10 mL of EtOH. Then 3 mL of $NH_2NH_2{\cdot}H_20$ were added dropwise. Thus, the reaction mixture was stirred at reflux for 12 hours. After cooling to room temperature, the solvents were removed under reduced pressure and the residue was dissolved in $CHCl_3$. The organic phase was washed with water, brine and dried over magnesium sulfate. After purification by flash chromatography (100% EtOAc) 60.4 mg of **3b** were obtained as a white solid (33% yield).

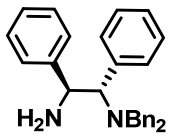
$[\alpha]^{20}_D$ = + 7.5 (*c* = 1.208, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31 – 7.07 (m, 15H), 3.99 (d, *J* = 7.1 Hz, 1H), 3.75 (d, *J* = 7.1 Hz, 1H), 3.67 (d, *J* = 13.3 Hz, 1H), 3.46 (d, *J* = 13.4 Hz, 1H), 1.89 (br s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 143.6, 141.4, 140.7, 128.4, 128.19, 128.16 (2C), 128.08, 127.1 (2C), 127.0, 126.9, 68.9, 62.0, 51.5.

HRMS (ESI): calculated for $C_{21}H_{23}N_2^+$, $[M+H]^+$ = 303.1856; found = 303.1880.

(1*S*,2*S*)-*N*1,*N*1-Dibenzyl-1,2-diphenylethane-1,2-diamine (3c)



3c

86.4 mg (0.165 mmol) of **S3** were dissolved in 5 mL of EtOH. Then 0.8 mL of $NH_2NH_2{\cdot}H_20$ were added dropwise. Thus, the reaction mixture was stirred at reflux for 12 hours. After cooling to room temperature, the solvents were removed under reduced pressure and the residue was dissolved in $CHCl_3$. The organic phase was washed with water, brine and dried over magnesium sulfate. After purification by flash chromatography (100% EtOAc) 59.2 mg of **3c** were obtained as a white solid (91% yield).

$[\alpha]^{20}_D$ = + 127 (*c* = 1.184, $CHCl_3$).

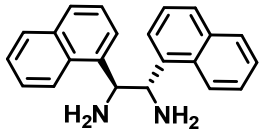
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48 – 7.31 (m, 8H), 7.30 – 7.10 (m, 5H), 7.07 – 6.93 (m, 7H), 4.58 (d, *J* = 10.6 Hz, 1H), 4.05 (d, *J* = 13.6 Hz, 2H), 3.86 (d, *J* = 10.6 Hz, 1H), 3.10 (d, *J* = 13.6 Hz, 2H), 2.17 (br s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 139.7, 134.9, 130.1, 129.0, 128.6, 128.1 (2C), 127.8, 127.2 (2C), 126.9, 69.1, 56.0, 54.1.

HRMS (ESI): calculated for $C_{28}H_{29}N_2^+$, $[M+H]^+$ = 393.2325; found = 393.2317.

5.3 Synthesis of the diamine catalysts (3d-f)[6]

(1*S*,2*S*)-1,2-Di(naphthalen-1-yl)ethane-1,2-diamine (3d)

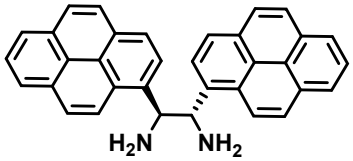


3d

In a 100 mL round-bottom flask, 1.0 g (4.093 mmol) of commercially available 1,2-bis(2-hydroxylphenyl)-1,2-diaminoethane were dissolved in 20 mL of DMSO and 9.6 mmol of 1-naphthaldehyde were added. The reaction mixture was stirred overnight at room temperature; thus, 50 mL of water were added. After addition of diethyl ether the organic phase was separated and the aqueous one was extracted with diethyl ether. The reunited organic phase was washed with brine twice and dried over sodium sulfate. After evaporation of the solvent, the yellow residue was dissolved in THF (28 mL) and diethyl ether (14 mL) and the resulting solution was separated in 7 different vials. To each of them 0.13 mL of 12 M HCl solution were added. Stirring the reaction mixture at ambient temperature overnight afforded the dihydrochloride product as a white precipitate that was collected by filtration. After basic workup of the obtained salt with 1 M NaOH solution in DCM the product can be extracted as the corresponding diamine. The organic phase was washed with brine and dried over sodium sulfate. After removal of the solvents under reduced pressure 1013.9 mg of catalyst **3d** were obtained as a white solid (79% yield). (Alternatively, after 12 M HCl solution addition and overnight stirring, it is possible to perform the basic workup and the residue obtained after extraction can be purified by flash chromatography employing *Biotage® NH-KP* columns (gradient: 0% to 100% of ethyl acetate in cyclohexane) or *SCX* columns).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.4 Hz, 2H), 7.88 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.82 – 7.74 (m, 4H), 7.62 – 7.44 (m, 6H), 5.12 (s, 2H), 1.76 (br s, 4H).

(1*S*,2*S*)-1,2-Di(pyren-1-yl)ethane-1,2-diamine (3e)



3e

In a 10 mL vial 100 mg (0.3889 mmol) of commercially available 1,2-bis(2-hydroxylphenyl)-1,2-diaminoethane were dissolved in 1.3 mL of EtOH and 0.9333 mmol of the corresponding arylaldehyde were added. The reaction mixture was stirred for 64 hours at room temperature and the resulting precipitate was collected by filtration. The latter was dissolved in 5 mL of THF and 0.15 mL of 12 M HCl solution were added. Stirring the reaction mixture at ambient temperature overnight afforded the dihydrochloride product as a pale yellow

precipitate that was collected by filtration. After basic workup of the obtained salt with 1 M NaOH solution in $CHCl_3$ the product was extracted as the corresponding diamine. The organic phase was washed with brine and dried over sodium sulfate. After removal of the solvents under reduced pressure 93.5 mg of catalyst **3e** were obtained as a pale yellow solid (52% yield).

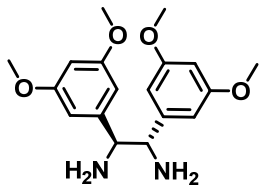
$[\alpha]^{20}_D$ = + 3.9 (*c* = 0.29, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.57 (d, *J* = 9.4 Hz, 2H), 8.31 (d, *J* = 8.0 Hz, 2H), 8.17 – 8.08 (m, 8H), 8.00 – 7.93 (m, 6H), 5.52 (s, 2H), 1.93 (br s, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 137.7, 131.5, 130.8, 130.5, 128.1, 127.7, 127.6, 127.3, 126.0, 125.3, 125.13, 125.12, 125.07, 124.99, 124.61, 122.6, 56.4.

HRMS (ESI): calculated for $C_{34}H_{25}N_2^+$, $[M+H]^+$ = 461.2012; found = 461.2044.

(1*S*,2*S*)-1,2-bis(3,5-Dimethoxyphenyl)ethane-1,2-diamine (3f)



3f

In a 10 mL vial 100 mg (0.3889 mmol) of commercially available 1,2-bis(2-hydroxylphenyl)-1,2-diaminoethane were dissolved in 1.3 mL of EtOH and 0.9333 mmol of the corresponding arylaldehyde were added. The reaction mixture was stirred for 64 hours at room temperature and the solvent removed under reduced pressure. The residue was dissolved in DCM, washed with brine and dried over sodium sulfate. After removal of the solvents under reduced pressure the residue was dissolved in 5 mL of THF and 0.15 mL of 12 M HCl solution were added. Stirring the reaction mixture at ambient temperature overnight afforded the dihydrochloride product as a pale yellow precipitate that was collected by filtration. After basic workup of the obtained salt with 1 M NaOH solution in $CHCl_3$ the product was extracted as the corresponding diamine. The organic phase was washed with brine and dried over sodium sulfate. After removal of the solvents under reduced pressure 87.2 mg of catalyst **3f** were obtained as a pale yellow solid (67% yield).

$[\alpha]^{20}_D$ = - 53.7 (*c* = 1.15, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.49 (d, *J* = 2.3 Hz, 4H), 6.34 (t, *J* = 2.3 Hz, 2H), 4.04 (s, 2H), 3.76 (s, 12H), 1.56 (br s, 4H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 160.8, 146.1, 105.0, 99.2, 61.8, 55.4.

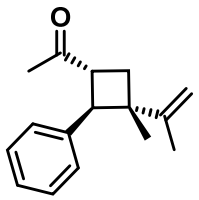
HRMS (ESI): calculated for $C_{18}H_{25}N_2O_4^+$, $[M+H]^+$ = 333.1809; found = 333.1792.

5.4 General procedure for the enantioselective [2+2] photocycloaddition

An oven-dried 10 mL vial, equipped with a magnetic stir bar, was charged with catalyst **3d** (0.02 mmol), and the corresponding ketone **1** (0.10 mmol). Then, 200 μL of a TFA solution (0.10 mmol, 0.5 M) in diethyl ether were added, followed by the corresponding alkene partner (0.30 mmol). The vial was closed with a PTFE/rubber septum and the reaction mixture was deoxygenated by three cycles of "freeze-pump-thaw". The reaction mixture was stirred at room temperature under blue LED irradiation (450 nm) in a photoreactor, as illustrated in the reaction setup, until reaction completion (as judged by TLC or ^{1}H NMR). The solvent was removed under reduced pressure and the crude mixture was purified by flash chromatography to afford the corresponding cyclobutane **4** in stated yield (sum of both major and minor diastereoisomers) and enantiomeric purity. Unless otherwise noted, characterization data and enantiomeric ratios are reported for the major cyclobutane diastereoisomer.

5.5 Characterization data for the enantioenriched cyclobutanes (4a-q)

1-((1*R*,2*R*,3*S*)-3-Methyl-2-phenyl-3-(prop-1-en-2-yl)cyclobutyl)ethan-1-one (4a)



4a

1a was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 22.6 mg of product as a colorless oil (99% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IB-3 column: CO_2/MeOH 95:5, flow rate 1.0 mL/min, λ = 210 nm, τ_{major} = 2.78 min, τ_{minor} = 2.59 (*er* = 90:10).

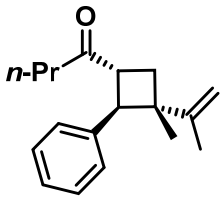
$[\alpha]^{20}_D$ = - 82 (*c* = 0.37, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 – 7.29 (m, 2H), 7.28 – 7.20 (m, 3H), 4.83 (br s, 1H), 4.79 (br p, *J* = 1.4 Hz, 1H), 3.73 (d, *J* = 10.2 Hz, 1H), 3.50 (q, *J* = 9.7 Hz, 1H), 2.31 (t, *J* = 10.2 Hz, 1H), 2.05 (s, 3H), 1.92 (dd, *J* = 10.8, 8.7 Hz, 1H), 1.71 (br s, 3H), 1.03 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 209.3, 152.6, 139.5, 128.4, 128.3, 126.7, 108.9, 50.2, 44.9, 44.8, 33.1, 28.4, 21.7, 19.0.

HRMS (ESI): calculated for $C_{16}H_{21}O^+$, $[M+H]^+$ = 229.1587; found = 229.1595.

1-((1*R*,2*R*,3*S*)-3-Methyl-2-phenyl-3-(prop-1-en-2-yl)cyclobutyl)butan-1-one (4b)



4b

4b was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 97 : 3) to obtain 25.4 mg of product as a colorless oil (99% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IC column: CO_2/MeOH 95:5, flow rate 2.0 mL/min, $\lambda = 230$ nm, $\tau_{major} = 6.85$ min, $\tau_{minor} = 6.63$ (*er* = 88:12).

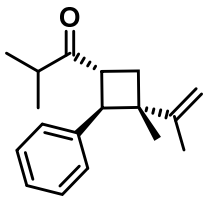
$[\alpha]^{20}_D = -86$ (*c* = 0.40, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37 – 7.28 (m, 2H), 7.27 – 7.20 (m, 3H), 4.83 (br s, 1H), 4.79 (br p, *J* = 1.5 Hz, 1H), 3.74 (d, *J* = 10.1 Hz, 1H), 3.49 (q, *J* = 9.7 Hz, 1H), 2.36 – 2.24 (m, 3H), 1.90 (dd, *J* = 10.6, 8.8 Hz, 1H), 1.71 (s, 3H), 1.55 (sxt, *J* = 7.3 Hz, 2H), 1.03 (s, 3H), 0.84 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 211.2, 152.6, 139.7, 128.3 (2C), 126.7, 108.9, 50.0, 44.9, 44.1, 43.2, 33.2, 21.7, 19.0, 17.2, 13.9.

HRMS (ESI): calculated for $C_{18}H_{25}O^+$, $[M+H]^+ = 257.1900$; found = 257.1902.

2-Methyl-1-((1*R*,2*R*,3*S*)-3-methyl-2-phenyl-3-(prop-1-en-2-yl)cyclobutyl)propan-1-one (4c)



4c

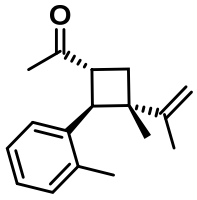
4c was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 97 : 3) to obtain 19.5 mg of product (as a mixture of diastereoisomers) as a colorless oil (76% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IA column: CO_2/MeOH 95:5, flow rate 1.0 mL/min, $\lambda = 210$ nm, $\tau_{major} = 12.16$ min, $\tau_{minor} = 11.57$ (*er* = 73:27).

^{1}H NMR (300 MHz, $CDCl_3$, *major diastereoisomer*): δ 7.34 – 7.18 (m, 5H), 4.83 (br s, 1H), 4.78 (br p, *J* = 1.5 Hz, 1H), 3.81 (d, *J* = 10.0 Hz, 1H), 3.64 (q, *J* = 9.5 Hz, 1H), 2.55 (hept, *J* = 7.2 Hz, 1H), 2.28 (t, *J* = 10.0 Hz, 1H), 1.92 (dd, *J* = 10.7, 8.6 Hz, 1H), 1.71 (s, 3H), 1.07 – 1.00 (m, 9H).

^{13}C NMR (75 MHz, $CDCl_3$, *major diastereoisomer*): δ 214.7, 152.6, 139.8, 128.30, 128.28, 126.6, 108.9, 49.6, 45.0, 42.4, 39.6, 34.1, 21.8, 19.0, 18.6, 18.2.

HRMS (ESI): calculated for $C_{18}H_{25}O^+$, $[M+H]^+ = 257.1900$; found = 257.1880.

1-((1*R*,2*S*,3*S*)-3-Methyl-3-(prop-1-en-2-yl)-2-(o-tolyl)cyclobutyl)ethan-1-one (4d)



4d

4d was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 22.5 mg of product as a colorless oil (93% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IC column: CO_2/MeOH 95:5, flow rate 2.0 mL/min, λ = 210 nm, τ_{major} = 7.84 min, τ_{minor} = 7.34 (*er* = 88:12).

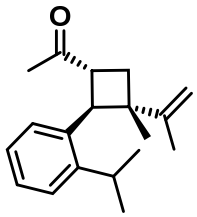
$[\alpha]^{20}_D$ = - 93 (*c* = 0.175, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.16 (m, 1H), 7.15 – 7.12 (m, 2H), 4.78 (br p, *J* = 1.5 Hz, 1H), 4.76 – 4.74 (m, 1H), 3.88 (d, *J* = 10.3 Hz, 1H), 3.60 (q, *J* = 9.3 Hz, 1H), 2.57 – 2.49 (m, 1H), 2.26 (s, 3H), 2.00 (s, 3H), 1.81 – 1.80 (m, 3H), 1.76 (dd, *J* = 11.2, 8.9 Hz, 1H), 1.07 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 209.2, 151.3, 137.29, 137.26, 130.7, 127.6, 126.6, 125.7, 110.1, 47.3, 45.1, 44.5, 31.3, 28.6, 21.5, 20.3, 19.7.

HRMS (ESI): calculated for $C_{17}H_{23}O^+$, $[M+H]^+$ = 243.1743; found = 243.1716.

1-((1*R*,2*S*,3*S*)-2-(2-Isopropylphenyl)-3-methyl-3-(prop-1-en-2-yl)cyclobutyl)ethan-1-one (4e)



4e

4e was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 25.4 mg of product as a colorless oil (94% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IC column: CO_2/MeOH 96:4, flow rate 2.0 mL/min, λ = 210 nm, τ_{major} = 5.94 min, τ_{minor} = 5.67 (*er* = 91:9).

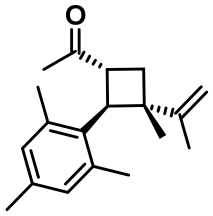
$[\alpha]^{20}_D$ = - 177 (*c* = 0.885, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 – 7.32 (m, 1H), 7.30 – 7.15 (m, 3H), 4.80 (br p, *J* = 1.5 Hz, 1H), 4.72 (s, 1H), 3.93 (d, *J* = 10.2 Hz, 1H), 3.63 (q, *J* = 9.3 Hz, 1H), 3.05 (hept, *J* = 6.8 Hz, 1H), 2.59 – 2.49 (m, 1H), 2.00 (s, 3H), 1.80 – 1.71 (m, 4H), 1.18 (d, *J* = 6.8 Hz, 3H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.04 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 209.1, 150.7, 148.1, 135.4, 127.7, 127.0, 125.6, 125.4, 110.1, 46.6, 45.3, 44.7, 31.1, 28.6, 28.5, 25.5, 22.9, 21.5, 19.7.

HRMS (ESI): calculated for $C_{19}H_{27}O^+$, $[M+H]^+$ = 271.2056; found = 271.2056.

1-((1*R*,2*S*,3*S*)-2-Mesityl-3-methyl-3-(prop-1-en-2-yl)cyclobutyl)ethan-1-one (4f)



4f

4f was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 20.5 mg of product as a colorless oil (76% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IB column: CO_2/MeOH 95:5, flow rate 1.0 mL/min, $\lambda = 210$ nm, $\tau_{major} = 3.51$ min, $\tau_{minor} = 3.20$ (*er* = 81:19).

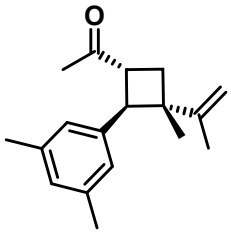
$[\alpha]^{20}_D = -103$ (*c* = 0.48, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.79 (s, 2H), 4.78 – 4.73 (m, 2H), 4.18 (dt, *J* = 10.7, 8.6 Hz, 1H), 4.04 (d, *J* = 10.8 Hz, 1H), 2.53 (dd, *J* = 11.2, 8.5 Hz, 1H), 2.43 (s, 6H), 2.22 (s, 3H), 2.05 (s, 3H), 1.84 (dd, *J* = 11.2, 8.8 Hz, 1H), 1.76 (s, 3H), 1.24 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 209.6, 151.5, 138.1, 135.8, 132.2, 130.9, 110.0, 49.1, 46.8, 46.2, 32.2, 28.0, 23.0, 21.7, 20.7, 20.5.

HRMS (ESI): calculated for $C_{19}H_{27}O^+$, $[M+H]^+ = 271.2056$; found = 271.2047.

1-((1*R*,2*R*,3*S*)-2-(3,5-Dimethylphenyl)-3-methyl-3-(prop-1-en-2-yl)cyclobutyl)ethan-1-one (4g)



4g

4g was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 22.1 mg of product as a colorless oil (86% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IB column: CO_2/MeOH 98:2, flow rate 1.0 mL/min, $\lambda = 210$ nm, $\tau_{major} = 3.68$ min, $\tau_{minor} = 3.37$ (*er* = 87:13).

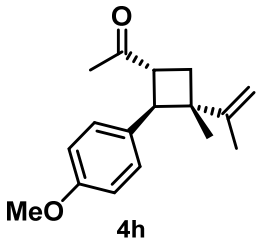
$[\alpha]^{20}_D = -115$ (*c* = 1.095, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.88 – 6.83 (m, 3H), 4.84 – 4.82 (m, 1H), 4.78 (br p, *J* = 1.4 Hz, 1H), 3.65 (d, *J* = 10.2 Hz, 1H), 3.47 (q, *J* = 9.6 Hz, 1H), 2.32 – 2.25 (m, 7H), 2.04 (s, 3H), 1.90 (dd, *J* = 10.7, 8.8 Hz, 1H), 1.71 – 1.70 (m, 3H), 1.03 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 209.4, 152.7, 139.4, 137.7, 128.4, 126.2, 108.8, 50.2, 44.9, 44.8, 33.1, 28.4, 21.7, 21.6, 19.0.

HRMS (ESI): calculated for $C_{18}H_{25}O^+$, $[M+H]^+ = 257.1900$; found = 257.1913.

1-((1*R*,2*R*,3*S*)-2-(4-Methoxyphenyl)-3-methyl-3-(prop-1-en-2-yl)cyclobutyl)ethan-1-one (4h)



4h

4h was prepared according to the general procedure (employing MTBE as the solvent) and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 15.5 mg of product as a colorless oil (60% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IA column: CO_2/MeOH 95:5, flow rate 2.0 mL/min, λ = 230 nm, τ_{major} = 8.37 min, τ_{minor} = 7.96 (*er* = 82:18).

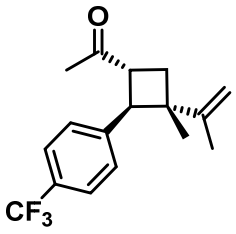
$[\alpha]^{20}_D$ = - 51 (*c* = 0.32, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.81 – 4.79 (m, 1H), 4.77 (br p, *J* = 1.4 Hz, 1H), 3.81 (s, 3H), 3.62 (d, *J* = 10.3 Hz, 1H), 3.44 (q, *J* = 9.5 Hz, 1H), 2.31 (t, *J* = 10.2 Hz, 1H), 2.02 (s, 3H), 1.93 – 1.84 (m, 1H), 1.69 (br s, 3H), 1.02 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 209.3, 158.5, 152.8, 131.6, 129.4, 113.8, 108.7, 55.4, 50.1, 45.3, 44.9, 32.8, 28.4, 21.7, 19.0.

HRMS (ESI): calculated for $C_{17}H_{23}O_2^+$, $[M+H]^+$ = 259.1693; found = 259.1659.

1-((1*R*,2*R*,3*S*)-3-Methyl-3-(prop-1-en-2-yl)-2-(4-(trifluoromethyl)phenyl)cyclobutyl)ethan-1-one (4i)



4i

4i was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 18.4 mg of product as a colorless oil (62% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IG-3 column: CO_2/MeOH 95:5, flow rate 2.0 mL/min, λ = 230 nm, τ_{major} = 2.66 min, τ_{minor} = 3.26 (*er* = 82:18).

$[\alpha]^{20}_D$ = - 40 (*c* = 0.175, $CHCl_3$).

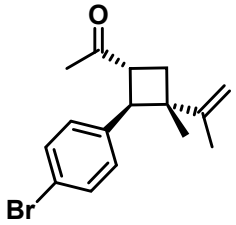
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 4.86 – 4.81 (m, 2H), 3.84 (d, *J* = 10.2 Hz, 1H), 3.49 (q, *J* = 9.6 Hz, 1H), 2.28 (t, *J* = 10.2 Hz, 1H), 2.09 (s, 3H), 2.00 (ddd, *J* = 10.7, 8.9, 0.8 Hz, 1H), 1.72 (dd, *J* = 1.4, 0.7 Hz, 3H), 1.03 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 208.7, 151.9, 143.83, 143.82, 128.4 (2C), 125.39, 125.34, 125.29, 125.24, 109.4, 49.0, 44.9, 44.8, 33.7, 28.2, 21.6, 19.0.

^{19}F NMR (282 MHz, $CDCl_3$): δ -62.44.

HRMS (ESI): calculated for $C_{17}H_{20}F_3O^+$, $[M+H]^+$ = 297.1461; found = 297.1430.

1-((1*R*,2*R*,3*S*)-2-(4-Bromophenyl)-3-methyl-3-(prop-1-en-2-yl)cyclobutyl)ethan-1-one (4j)



4j

4j was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 27.0 mg of product as a colorless oil (88% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IA column: CO_2/MeOH 95:5, flow rate 2.0 mL/min, λ = 230 nm, τ_{major} = 10.02 min, τ_{minor} = 9.59 (*er* = 88:12).

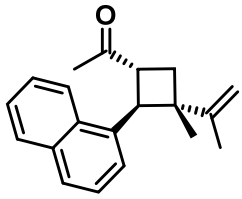
$[\alpha]^{20}_D$ = - 57 (*c* = 0.475, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.5 Hz, 2H), 4.83 – 4.76 (m, 2H), 3.70 (d, *J* = 10.2 Hz, 1H), 3.43 (q, *J* = 9.6 Hz, 1H), 2.28 (t, *J* = 10.2 Hz, 1H), 2.06 (s, 3H), 1.95 (dd, *J* = 10.8, 8.8 Hz, 1H), 1.72 – 1.69 (m, 3H), 1.01 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 208.8, 152.2, 138.6, 131.5, 129.9, 120.6, 109.1, 49.2, 44.9, 44.7, 33.4, 28.3, 21.6, 18.9.

HRMS (ESI): calculated for $C_{16}H_{23}NBrO^+$, $[M+NH_4]^+$ = 324.0958; found = 324.0926.

1-((1*R*,2*S*,3*S*)-3-Methyl-2-(naphthalen-1-yl)-3-(prop-1-en-2-yl)cyclobutyl)ethan-1-one (4k)



4k

4k was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 13.6 mg of product as a colorless oil (49% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IG-3 column: CO_2/MeOH 95:5, flow rate 2.0 mL/min, λ = 230 nm, τ_{major} = 7.73 min, τ_{minor} = 7.20 (*er* = 81:19).

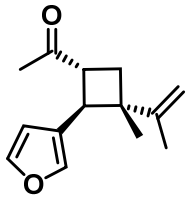
$[\alpha]^{20}_D$ = - 120 (*c* = 0.40, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 – 7.92 (m, 1H), 7.87 – 7.81 (m, 1H), 7.78 – 7.73 (m, 1H), 7.56 – 7.39 (m, 4H), 4.91 – 4.88 (m, 1H), 4.85 – 4.83 (m, 1H), 4.41 (d, *J* = 10.1 Hz, 1H), 3.79 (q, *J* = 9.4 Hz, 1H), 2.73 – 2.64 (m, 1H), 2.04 (s, 3H), 1.83 – 1.81 (m, 4H), 1.01 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 209.1, 150.9, 135.5, 134.1, 132.6, 128.7, 127.5, 125.9, 125.8, 125.2, 125.0, 124.7, 111.2, 47.5, 44.8, 44.7, 31.5, 28.6, 21.4, 20.3.

HRMS (ESI): calculated for $C_{20}H_{23}O^+$, $[M+H]^+$ = 279.1743; found = 279.1757.

1-((1*R*,2*S*,3*S*)-2-(Furan-3-yl)-3-methyl-3-(prop-1-en-2-yl)cyclobutyl)ethan-1-one (4l)



4l

4l was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 9.8 mg of product as a colorless oil (45% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IG-3 column: CO_2/MeOH 95:5, flow rate 2.0 mL/min, λ = 210 nm, τ_{major} = 3.97 min, τ_{minor} = 3.70 (*er* = 76:24).

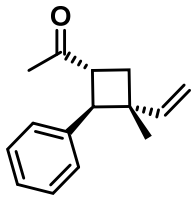
$[\alpha]^{20}_D$ = - 16 (*c* = 0.125, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.39 (t, *J* = 1.7 Hz, 1H), 7.36 – 7.31 (m, 1H), 6.34 (dd, *J* = 1.8, 0.9 Hz, 1H), 4.74 – 4.71 (m, 2H), 3.46 (d, *J* = 10.2 Hz, 1H), 3.26 – 3.15 (m, 1H), 2.27 (t, *J* = 10.3 Hz, 1H), 2.06 (s, 3H), 1.90 (ddd, *J* = 10.8, 8.5, 0.8 Hz, 1H), 1.67 (dd, *J* = 1.4, 0.8 Hz, 3H), 1.10 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 208.9, 152.89, 143.1, 140.1, 124.2, 111.0, 108.3, 46.2, 44.2, 42.1, 33.2, 28.4, 22.2, 18.4.

HRMS (ESI): calculated for $C_{14}H_{19}O_2^+$, $[M+H]^+$ = 219.1380; found = 219.1342.

1-((1*R*,2*S*,3*R*)-3-Methyl-2-phenyl-3-vinylcyclobutyl)ethan-1-one (4m)



4m

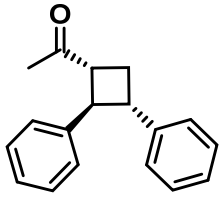
4m was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 16.5 mg of product (as a mixture of diastereoisomers) as a colorless oil (77% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IG-3 column: CO_2/MeOH 95:5, flow rate 2.0 mL/min, λ = 210 nm, τ_{major} = 4.10 min, τ_{minor} = 5.38 (*er* = 81:19).

^{1}H NMR (300 MHz, $CDCl_3$, *major diastereoisomer*): δ 7.36 – 7.12 (m, 5H), 6.04 (dd, *J* = 17.1, 10.8 Hz, 1H), 5.06 – 4.95 (m, 2H), 3.65 – 3.41 (m, 2H), 2.36 – 2.23 (m, 1H), 2.11 (s, 3H), 1.97 – 1.88 (m, 1H), 0.90 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, *major diastereoisomer*): δ 209.2, 147.0, 138.9, 128.4, 127.4, 126.7, 111.8, 51.2, 44.4, 41.7, 33.5, 28.5, 20.4.

HRMS (ESI): calculated for $C_{15}H_{19}O^+$, $[M+H]^+$ = 215.1430; found = 215.1442.

1-((1*R*,2*R*,3*S*)-2,3-Diphenylcyclobutyl)ethan-1-one (4n)



4n

4n was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 20.5 mg of product as a colorless oil (82% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IB-3 column: CO_2/MeOH 95:5, flow rate 1.0 mL/min, $\lambda = 210$ nm, $\tau_{major} = 6.40$ min, $\tau_{minor} = 5.88$ (*er* = 82:18).

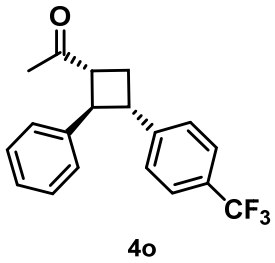
$[\alpha]^{20}_D = +2.3$ (*c* = 0.325, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38 – 7.16 (m, 10H), 3.68 (t, *J* = 9.6 Hz, 1H), 3.56 (td, *J* = 10.0, 8.0 Hz, 1H), 3.31 (td, *J* = 9.7, 8.2 Hz, 1H), 2.65 – 2.53 (m, 1H), 2.33 (q, *J* = 10.1 Hz, 1H), 2.08 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 208.5, 143.3, 142.3, 128.8, 128.6, 127.1, 127.0, 126.8, 126.7, 50.9, 50.1, 43.0, 28.52, 28.50.

HRMS (ESI): calculated for $C_{18}H_{19}O^+$, $[M+H]^+ = 251.1430$; found = 251.1401.

1-((1*R*,2*R*,3*S*)-2-Phenyl-3-(4-(trifluoromethyl)phenyl)cyclobutyl)ethan-1-one (4o)



4o

4o was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 22.9 mg of product as a colorless oil (72% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IC column: CO_2/MeOH 95:5, flow rate 2.0 mL/min, $\lambda = 230$ nm, $\tau_{major} = 6.89$ min, $\tau_{minor} = 6.48$ (*er* = 78:22).

$[\alpha]^{20}_D = -4.1$ (*c* = 0.455, $CHCl_3$).

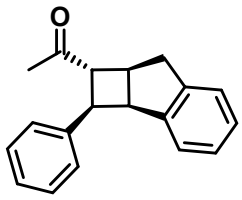
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.22 (m, 7H), 3.73 – 3.55 (m, 2H), 3.42 – 3.31 (m, 1H), 2.69 – 2.55 (m, 1H), 2.46 – 2.27 (m, 1H), 2.08 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 208.1, 147.26, 147.25, 141.7, 128.9, 127.3, 127.2, 127.0 (2C), 125.60, 125.55, 125.50, 125.45, 50.9, 50.0, 42.7, 28.6, 28.1.

^{19}F NMR (282 MHz, $CDCl_3$): δ -62.43.

HRMS (ESI): calculated for $C_{19}H_{21}NF_3O^+$, $[M+NH_4]^+ = 336.1570$; found = 336.1625.

1-((1*R*,2*R*,2a*R*,7a*S*)-2-phenyl-2,2a,7,7a-tetrahydro-1H-cyclobuta[a]inden-1-yl)ethan-1-one (4p)



4p

4p was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 11.2 mg of product (as a mixture of diastereoisomers) as a colorless oil (43% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IG-3 column: CO_2/MeOH 80:20, flow rate 2.0 mL/min, λ = 210 nm, τ_{major} = 3.06 min, τ_{minor} = 2.63 (*er* = 72:28).

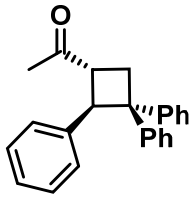
$[\alpha]^{20}_D$ = - 69 (*c* = 0.35, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$, *major diastereoisomer*): δ 7.29 (d, *J* = 7.8 Hz, 1H), 7.22 – 7.13 (m, 4H), 6.94 – 6.85 (m, 3H), 6.37 – 6.33 (m, 1H), 4.09 – 3.95 (m, 2H), 3.38 – 3.18 (m, 3H), 2.95 (d, *J* = 16.2 Hz, 1H), 2.02 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$, *major diastereoisomer*): δ 208.6, 144.1, 141.4, 138.9, 128.15, 128.08, 127.7, 127.3, 126.8, 126.1, 125.5, 55.3, 48.4, 46.2, 39.0, 36.6, 28.6.

HRMS (ESI): calculated for $C_{19}H_{19}O^+$, $[M+H]^+$ = 263.1430; found = 263.1440.

1-((1*R*,2*R*)-2,3,3-Triphenylcyclobutyl)ethan-1-one (4q)



4q

4q was prepared according to the general procedure and purified by flash chromatography (CyHex : EtOAc = 95 : 5) to obtain 24.5 mg of product as a white solid (75% yield). The enantiomeric excess was determined by SFC on a *Daicel Chiralpak* IB-3 column: CO_2/MeOH 95:5, flow rate 2.0 mL/min, λ = 210 nm, τ_{major} = 3.24 min, τ_{minor} = 2.85 (*er* = 81:19).

$[\alpha]^{20}_D$ = + 13 (*c* = 0.785, $CHCl_3$).

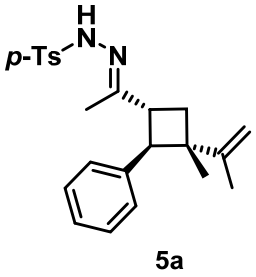
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 4H), 7.17 – 7.09 (m, 7H), 7.00 – 6.95 (m, 2H), 6.90 – 6.85 (m, 2H), 4.35 (d, *J* = 10.7 Hz, 1H), 3.59 (td, *J* = 10.6, 7.9 Hz, 1H), 3.24 (dd, *J* = 11.7, 7.9 Hz, 1H), 2.67 (dd, *J* = 11.8, 10.5 Hz, 1H), 1.93 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 208.5, 150.9, 141.6, 138.8, 129.0, 128.7, 128.5, 128.1, 127.9, 127.1, 126.31, 126.27, 126.0, 53.7, 53.4, 47.8, 32.6, 28.7.

HRMS (ESI): calculated for $C_{24}H_{26}NO^+$, $[M+H]^+$ = 327.1743; found = 327.1746.

5.6 Derivatization of 4a to 5a for X-Ray analysis

4-Methyl-*N*'-((*E*)-1-((1*R*,2*R*,3*S*)-3-methyl-2-phenyl-3-(prop-1-en-2-yl)cyclobutyl)ethylidene)benzenesulfonohydrazide



5a

0.1 mmol of **4a** (*er* of the sample = 82:18) were dissolved in ethanol (5 mL) and *para*-toluenesulfonyl hydrazide (0.15 mmol) were added. The reaction mixture was stirred overnight at room temperature and, after solvent removal, purified by flash chromatography (CyHex : EtOAc = 80 : 20) to obtain 31.9 mg of product as a white solid (80% yield).

$[\alpha]^{20}_D$ = - 32.1 (*c* = 0.910, $CHCl_3$).

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.19 (m, 3H), 7.17 – 7.09 (m, 4H), 4.82 – 4.80 (m, 1H), 4.79 – 4.76 (m, 1H), 3.63 (d, *J* = 10.1 Hz, 1H), 3.31 (q, *J* = 9.6 Hz, 1H), 2.38 (s, 3H), 2.11 (t, *J* = 10.2 Hz, 1H), 1.95 – 1.87 (m, 1H), 1.69 (s, 6H), 0.99 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0, 152.9, 143.8, 140.2, 135.3, 129.4, 128.24, 128.21, 128.1, 126.3, 108.6, 50.2, 45.2, 40.8, 34.6, 21.7, 21.4, 19.1, 14.0.

HRMS (ESI): calculated for $C_{23}H_{29}N_2O_2S^+$, $[M+H]^+$ = 397.1944; found = 397.1940.

6. NMR spectra

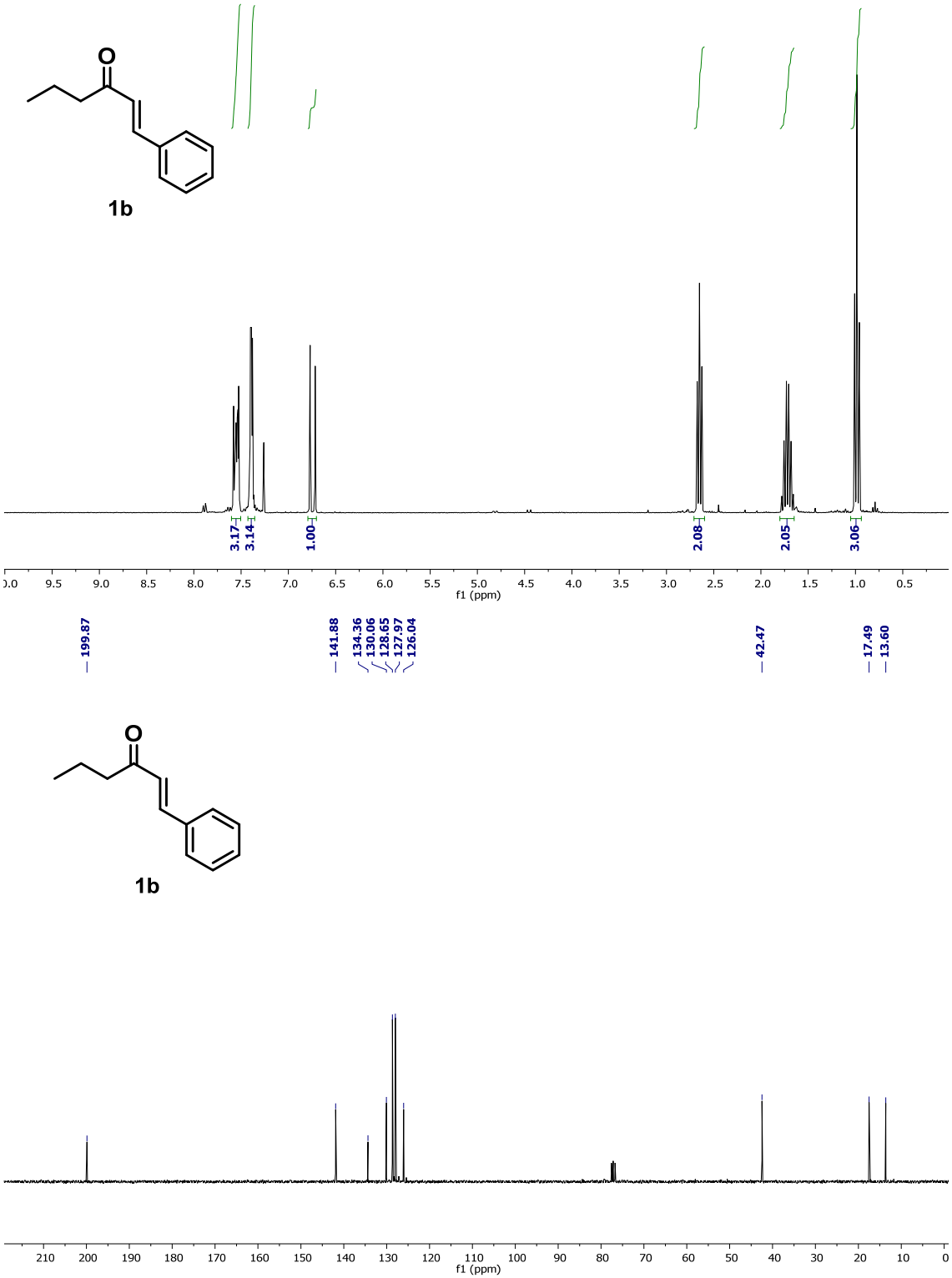


Figure S2: ^{1}H and ^{13}C NMR spectra for compound **1b** (300 and 75 MHz, $CDCl_3$, 298K).

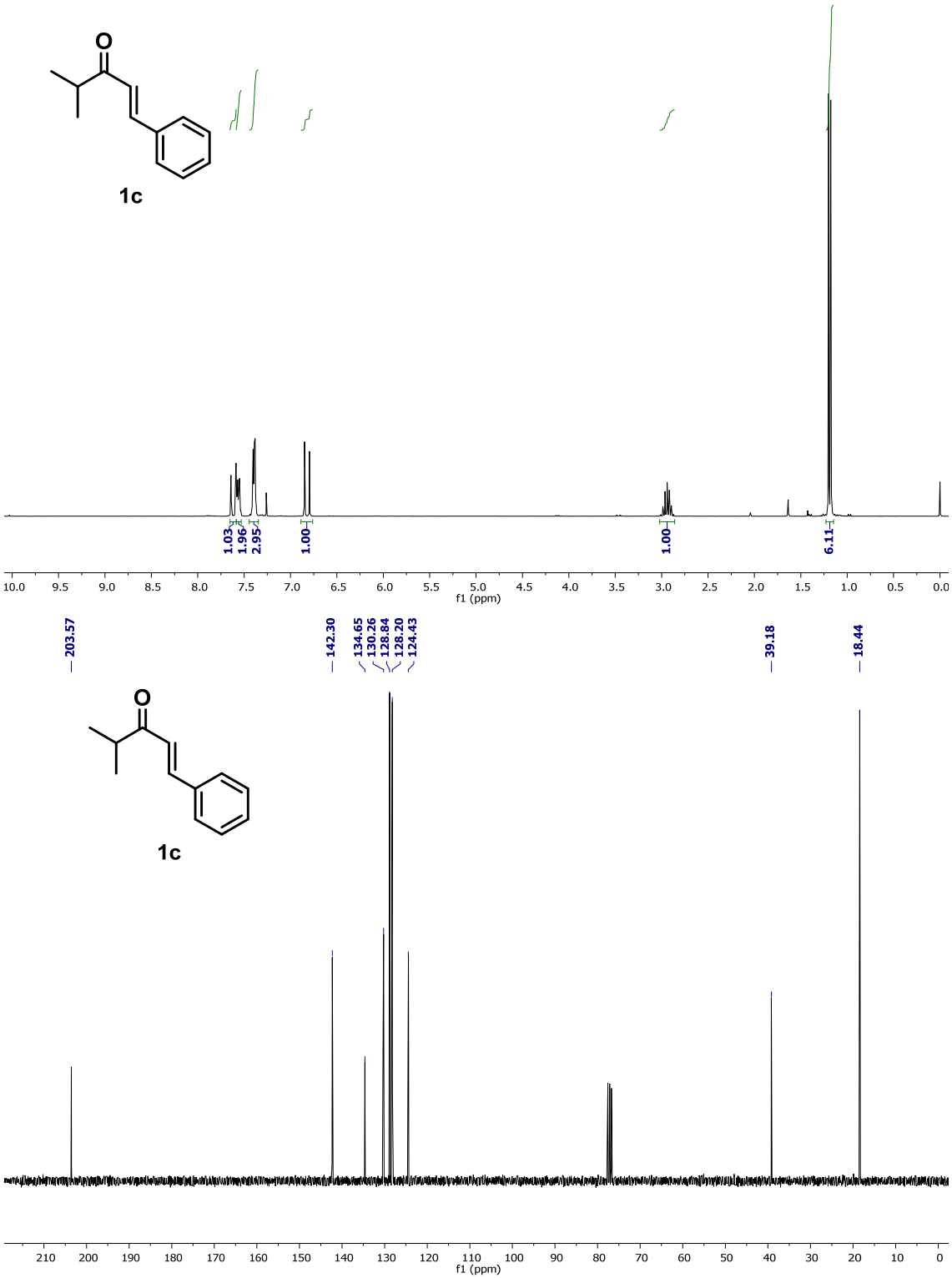


Figure S3: ^{1}H and ^{13}C NMR spectra for compound **1c** (300 and 75 MHz, $CDCl_3$, 298K).

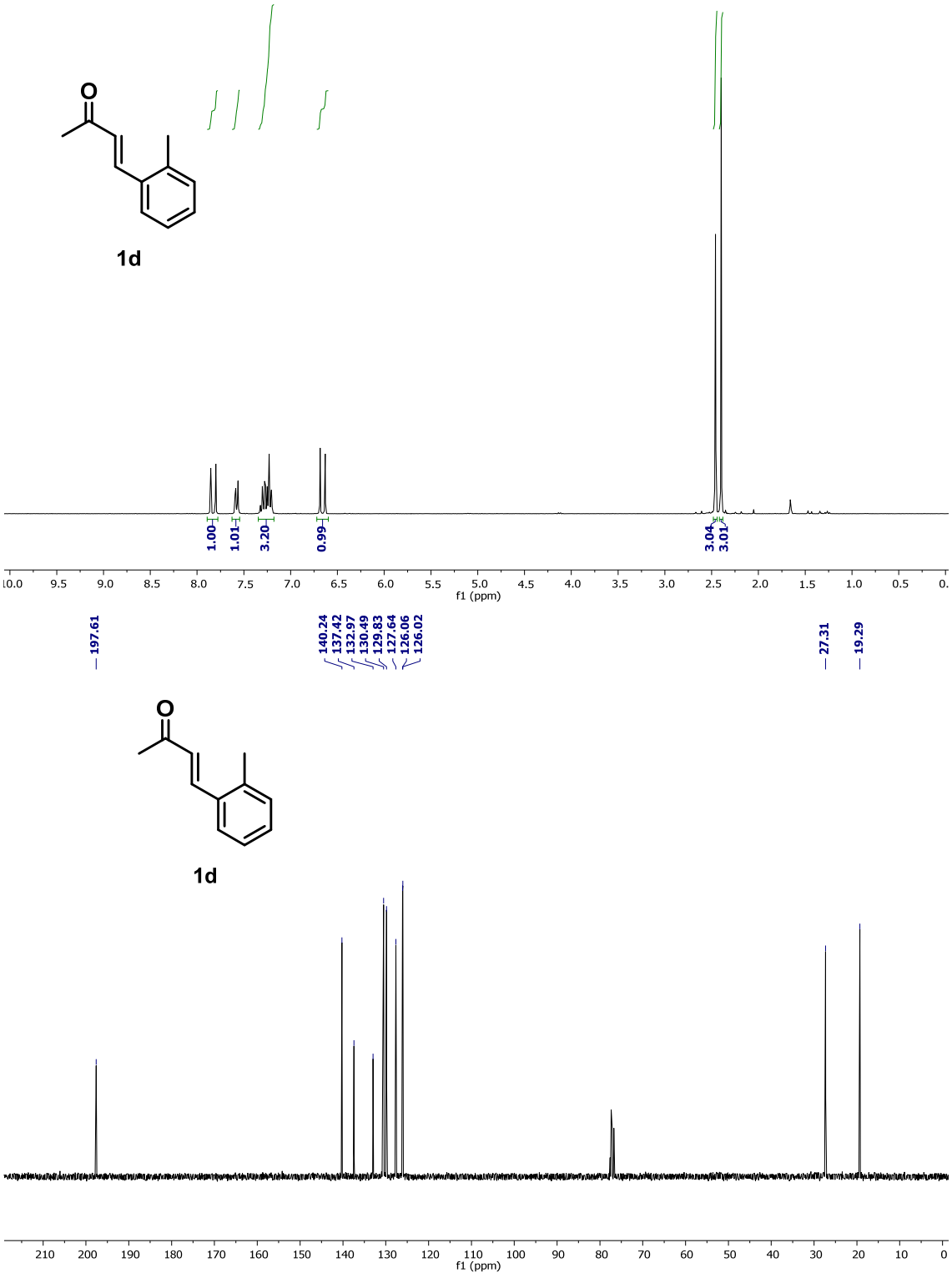


Figure S4: ^{1}H and ^{13}C NMR spectra for compound **1d** (300 and 75 MHz, $CDCl_3$, 298K).

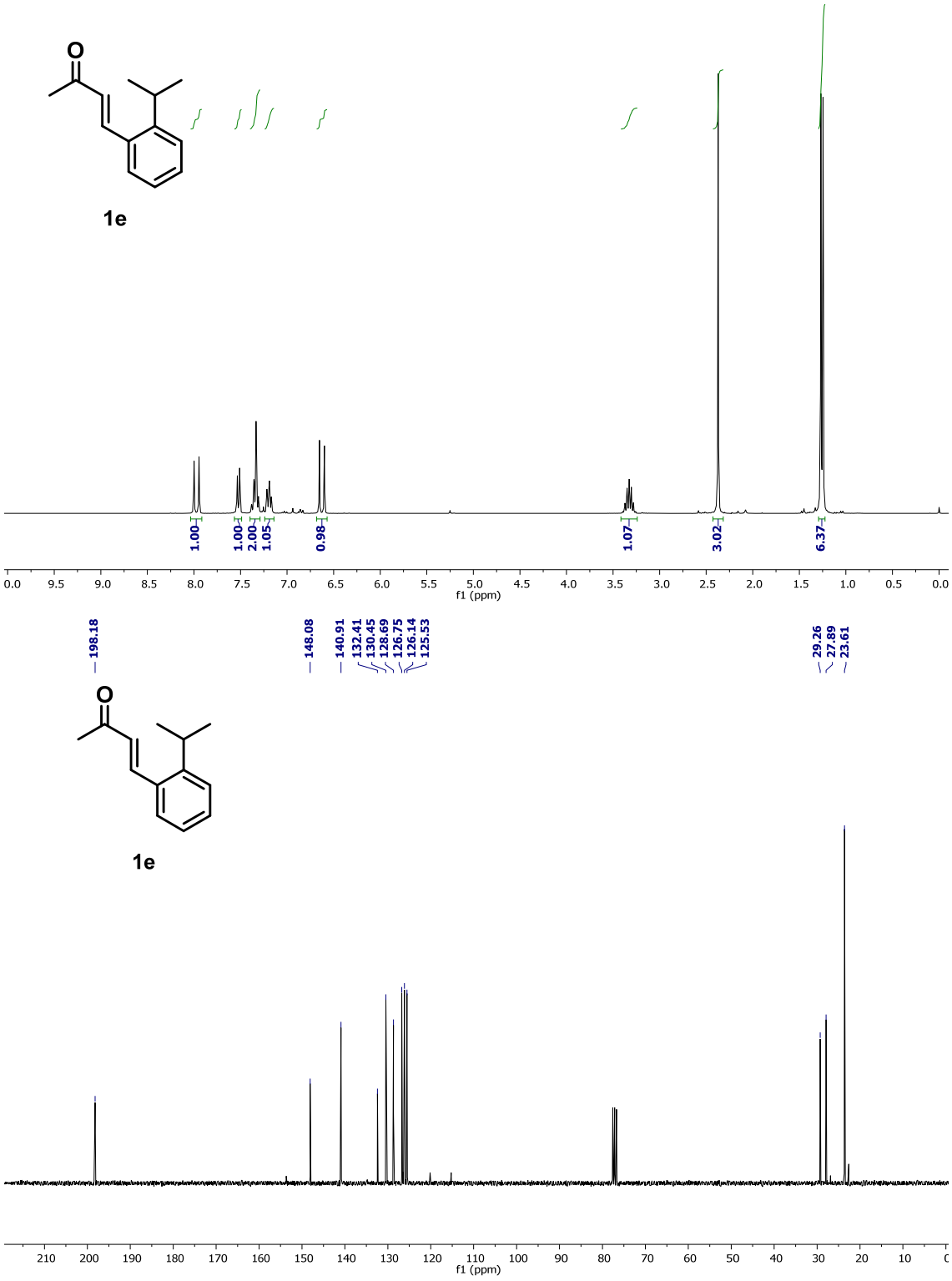


Figure S5: ^{1}H and ^{13}C NMR spectra for compound **1e** (300 and 75 MHz, $CDCl_3$, 298K).

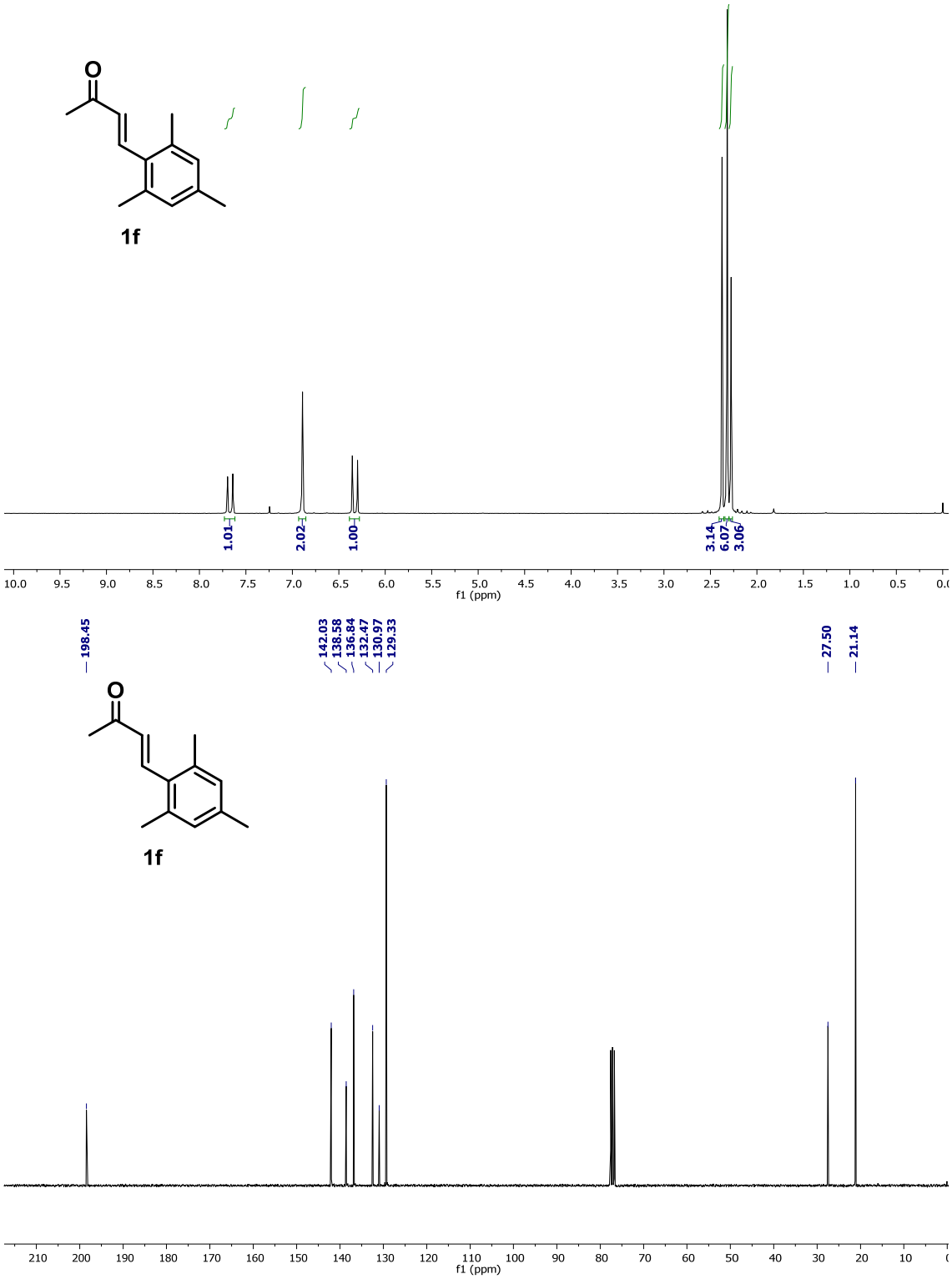


Figure S6: ^{1}H and ^{13}C NMR spectra for compound **1f** (300 and 75 MHz, $CDCl_3$, 298K).

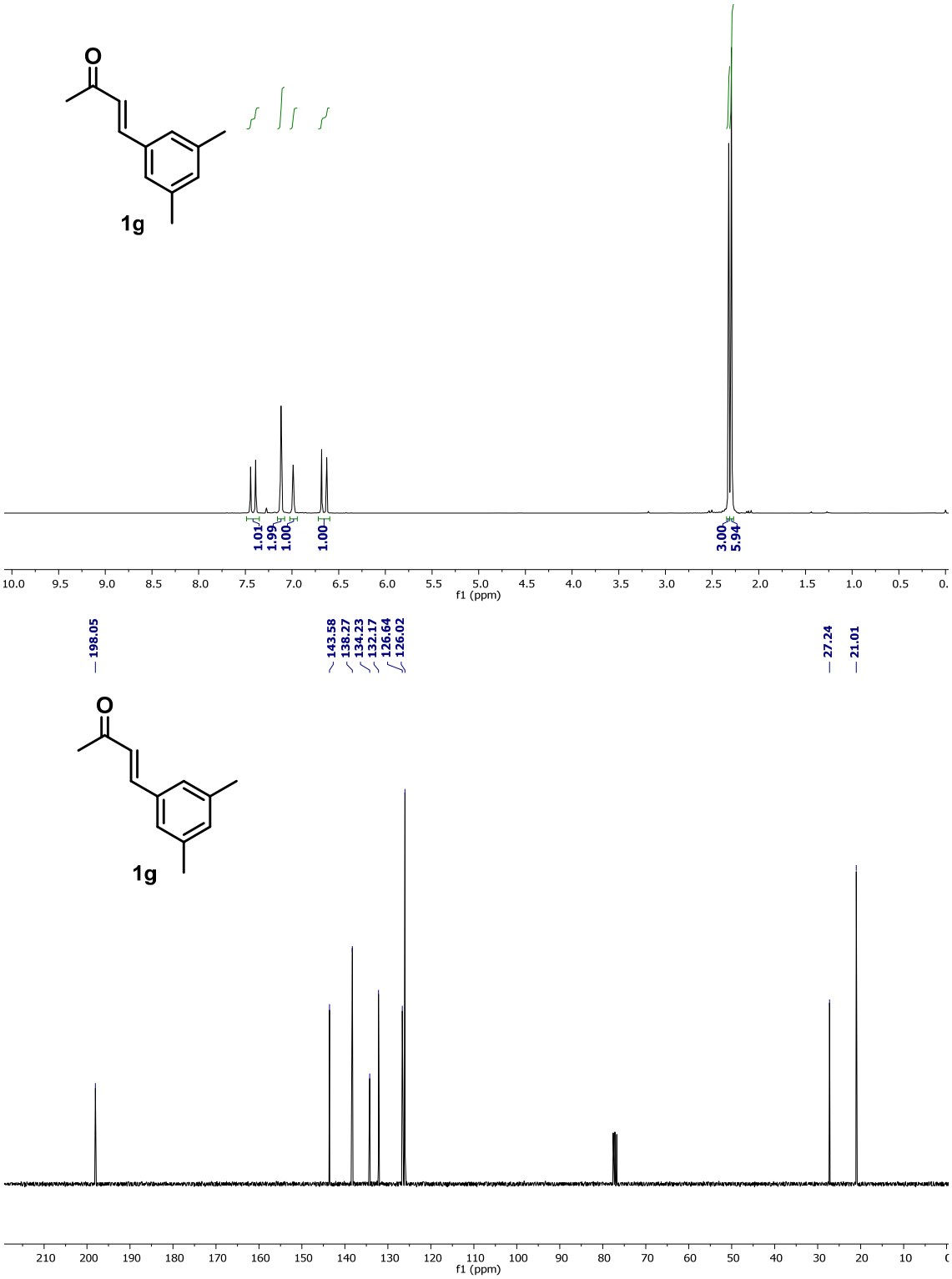


Figure S7: ^{1}H and ^{13}C NMR spectra for compound **1g** (300 and 75 MHz, $CDCl_3$, 298K).

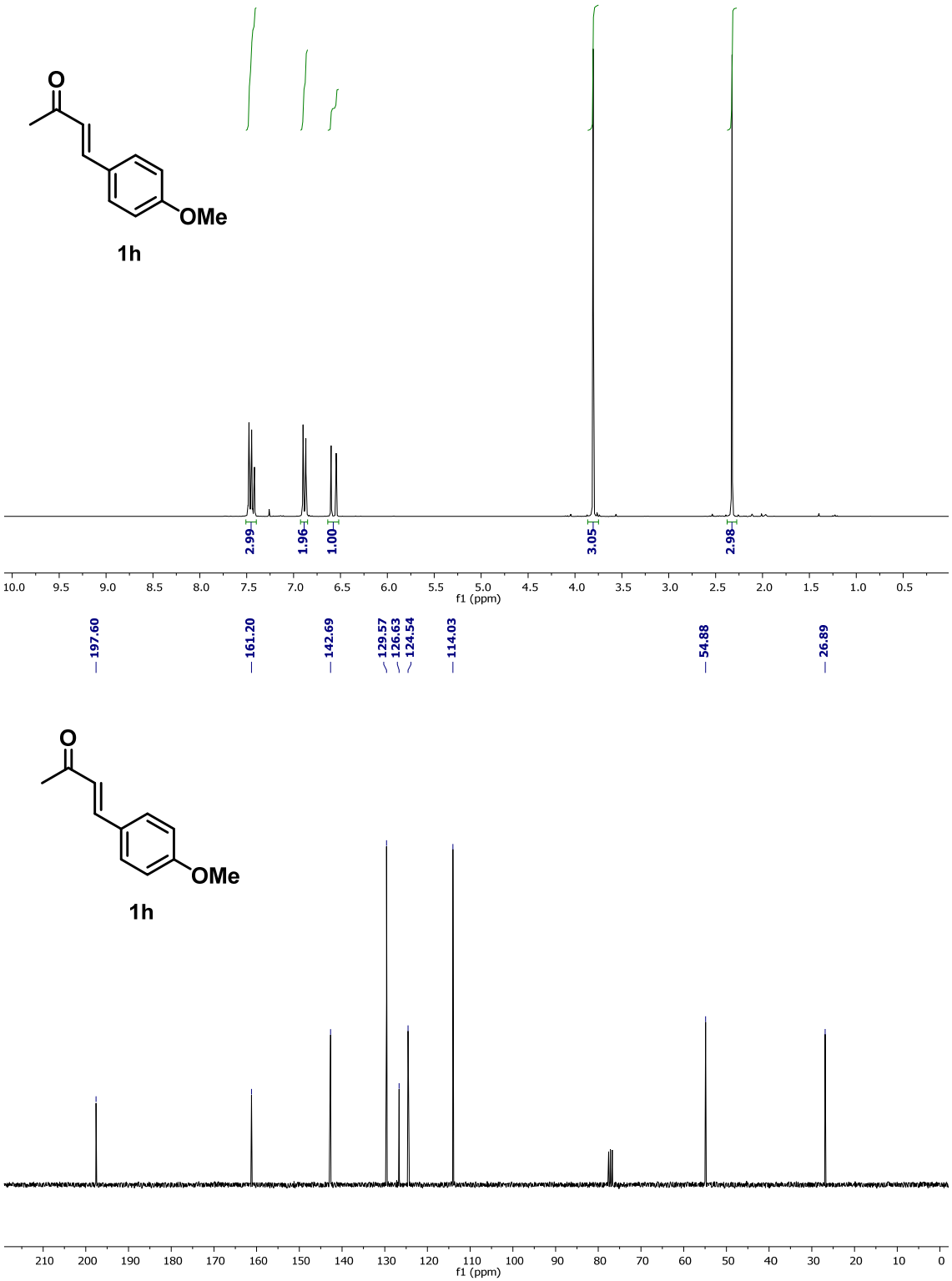


Figure S8: ^{1}H and ^{13}C NMR spectra for compound **1h** (300 and 75 MHz, $CDCl_3$, 298K).

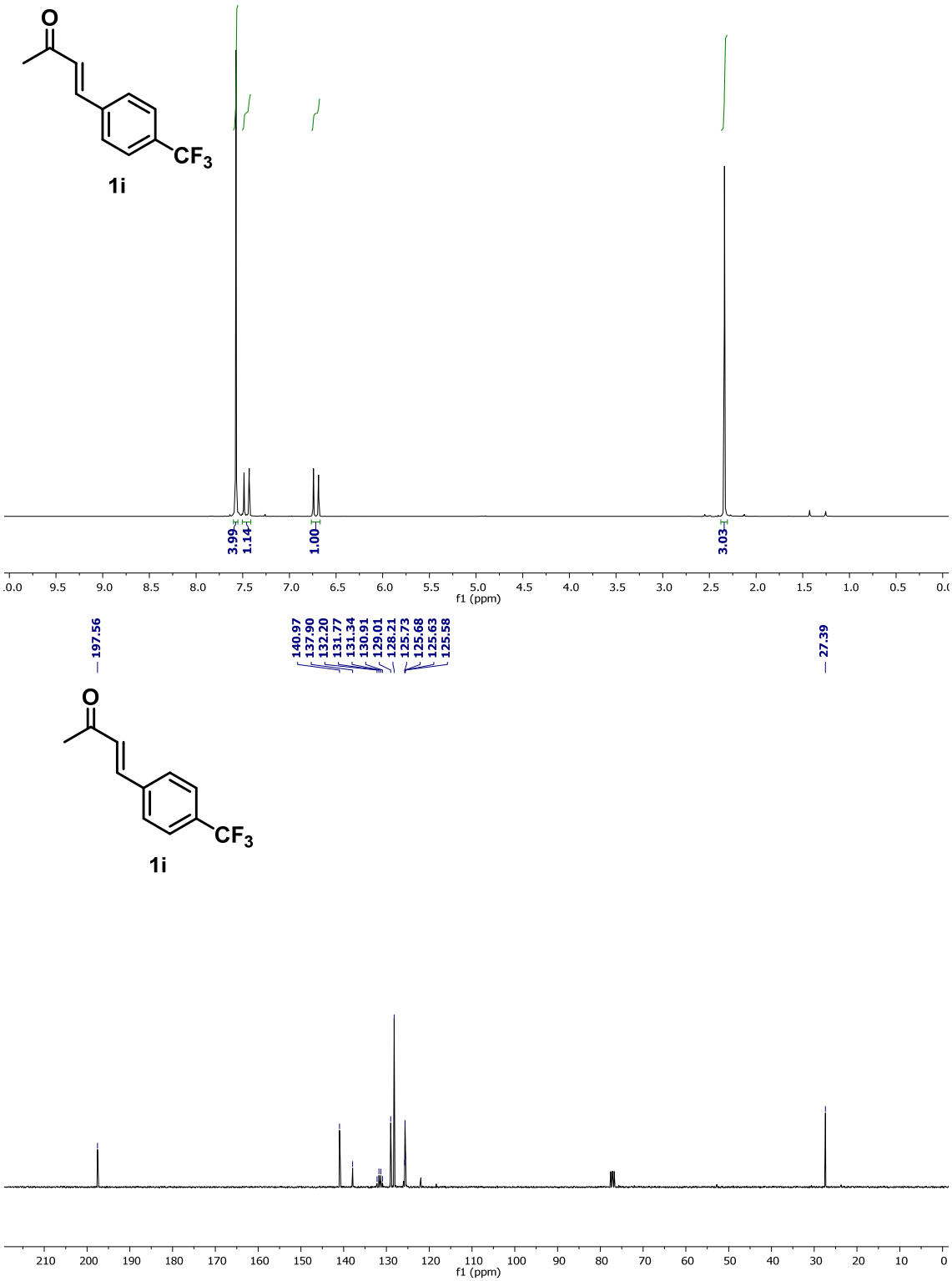


Figure S9: ^{1}H and ^{13}C NMR spectra for compound **1i** (300 and 75 MHz, $CDCl_3$, 298K).

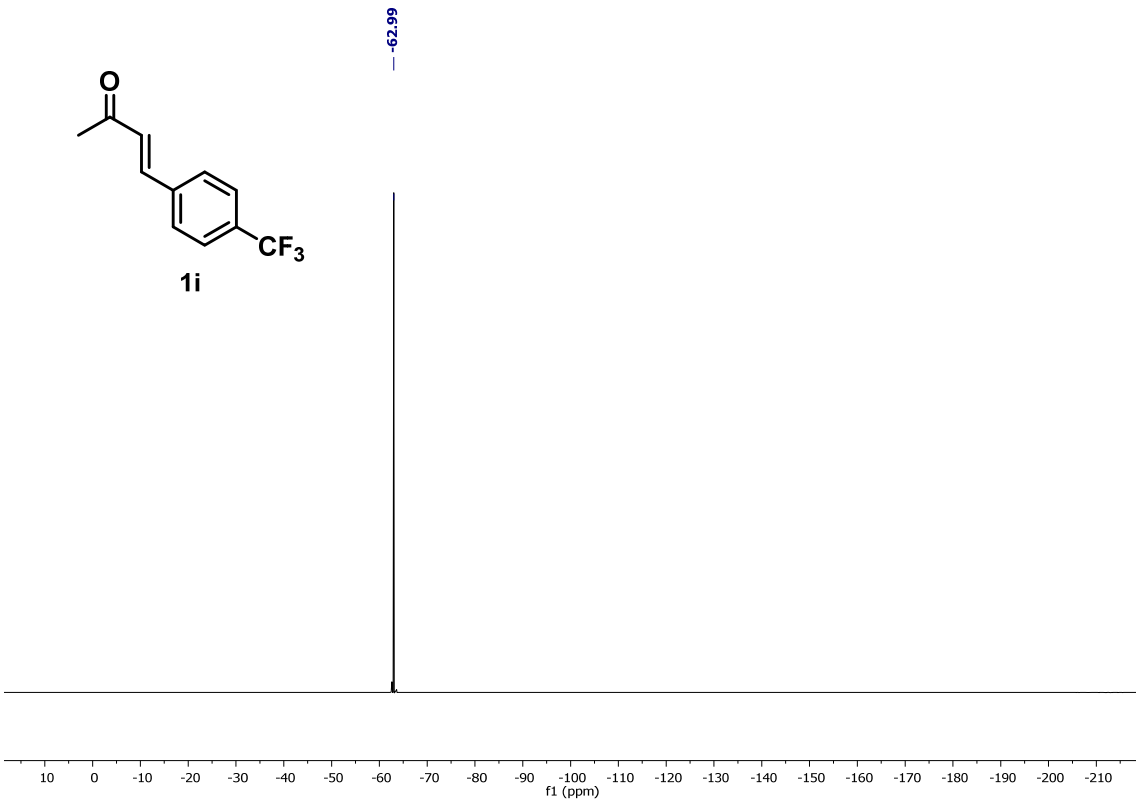


Figure S10: ^{19}F spectrum for compound **1i** (282 MHz, $CDCl_3$, 298K).

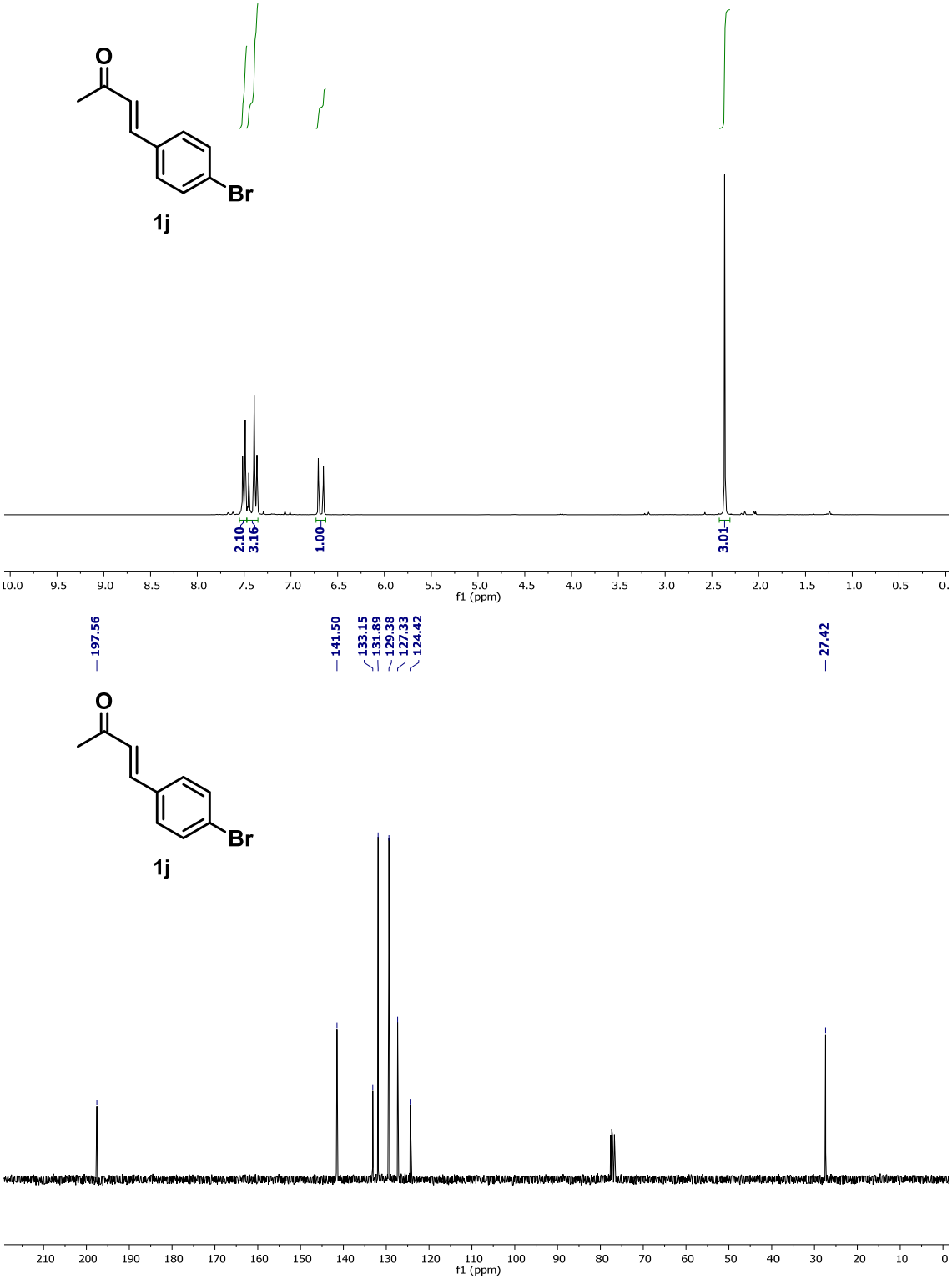


Figure S11: ^{1}H and ^{13}C NMR spectra for compound **1j** (300 and 75 MHz, $CDCl_3$, 298K).

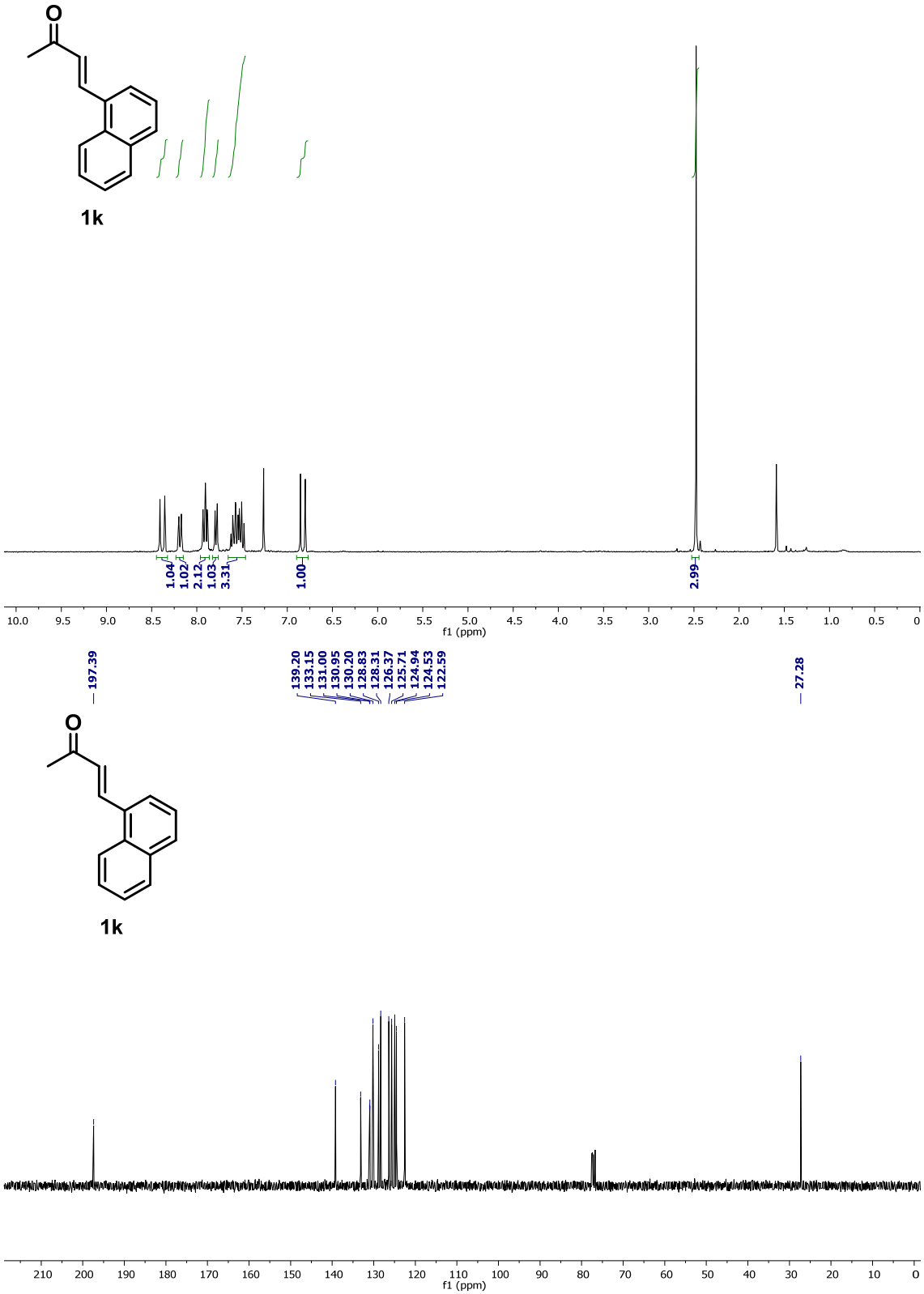


Figure S12: ^{1}H and ^{13}C NMR spectra for compound **1k** (300 and 75 MHz, $CDCl_3$, 298K).

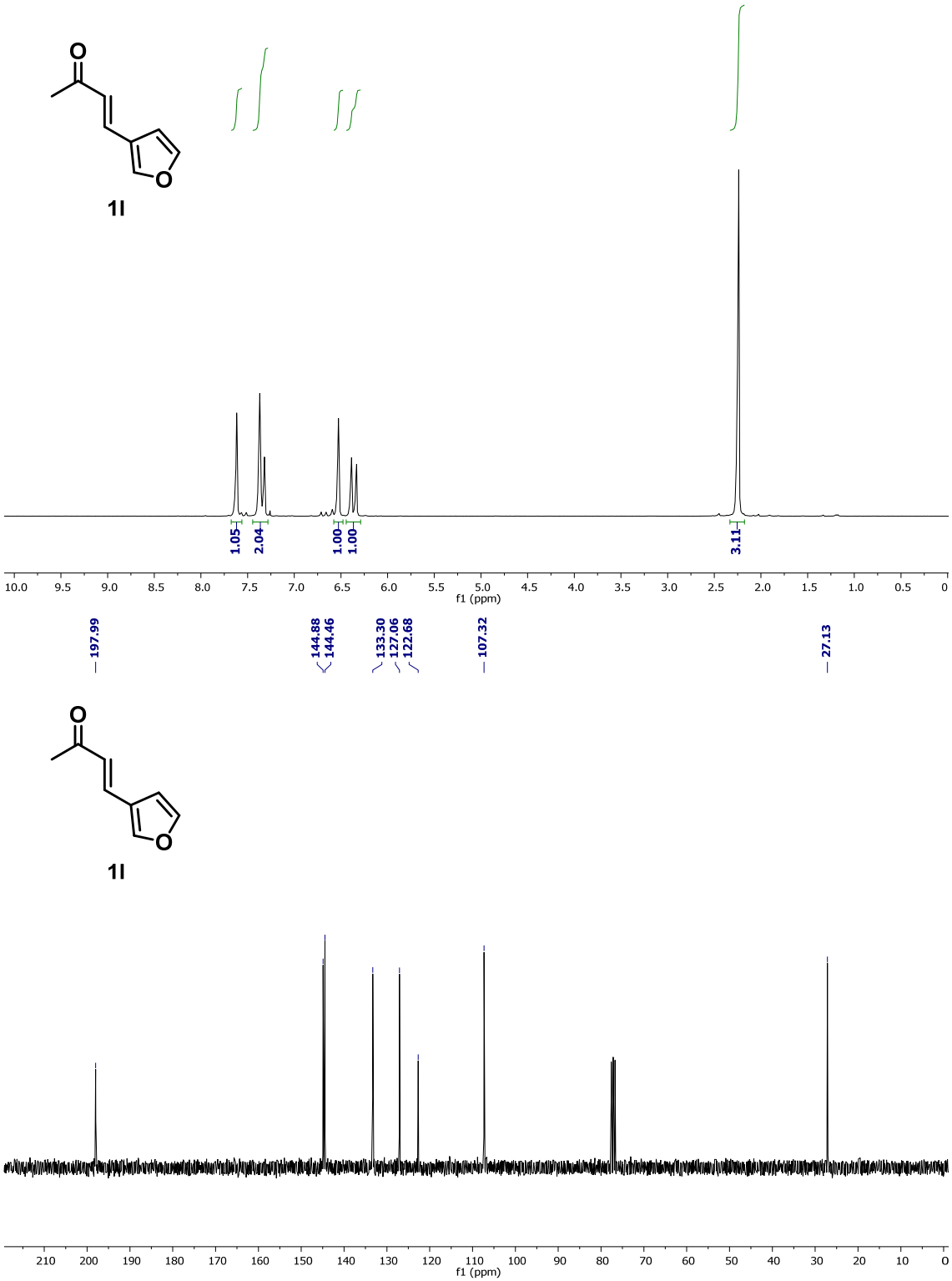


Figure S13: ^{1}H and ^{13}C NMR spectra for compound **1l** (300 and 75 MHz, $CDCl_3$, 298K).

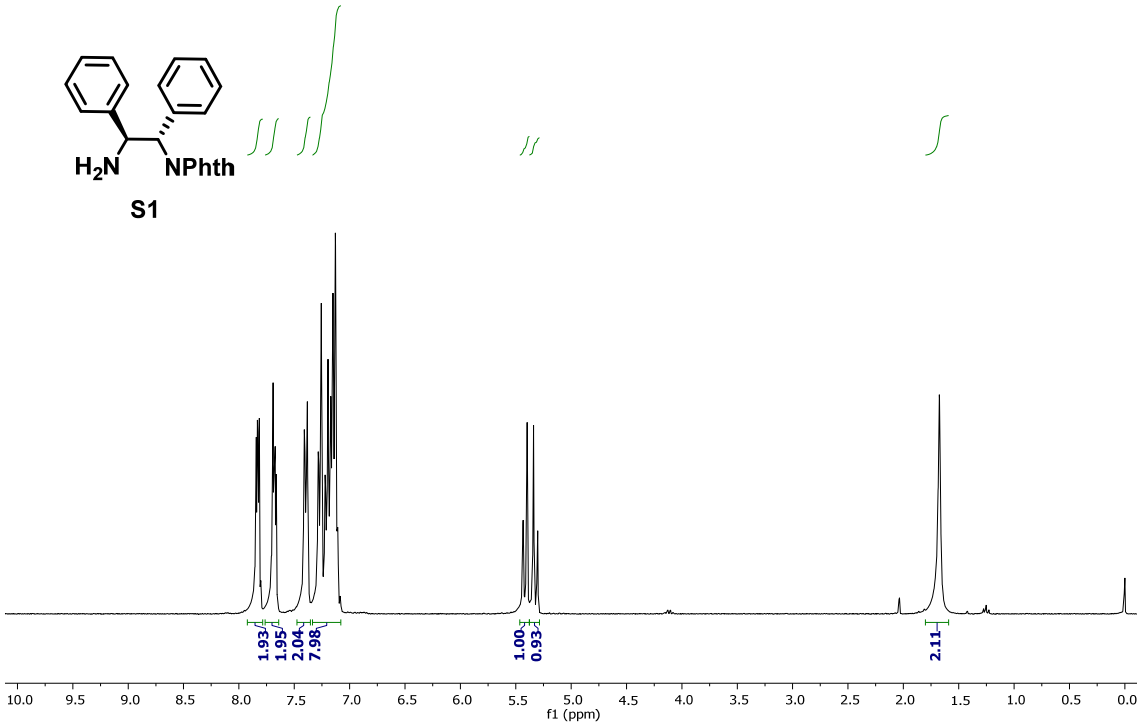


Figure S14: ^{1}H NMR spectrum for compound **S1** (300 MHz, $CDCl_3$, 298K).

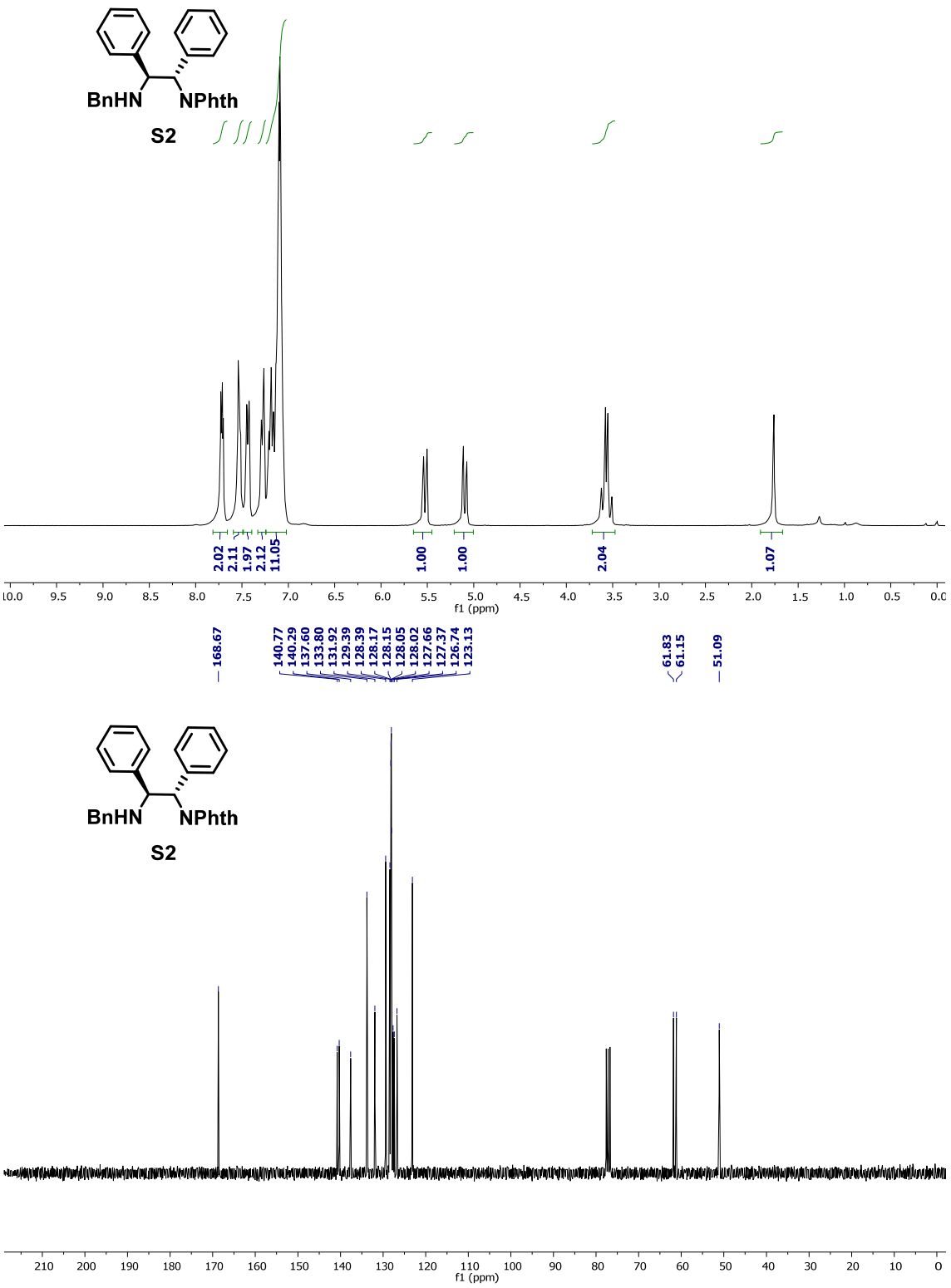


Figure S15: ^{1}H and ^{13}C NMR spectra for compound **S2** (300 and 75 MHz, $CDCl_3$, 298K).

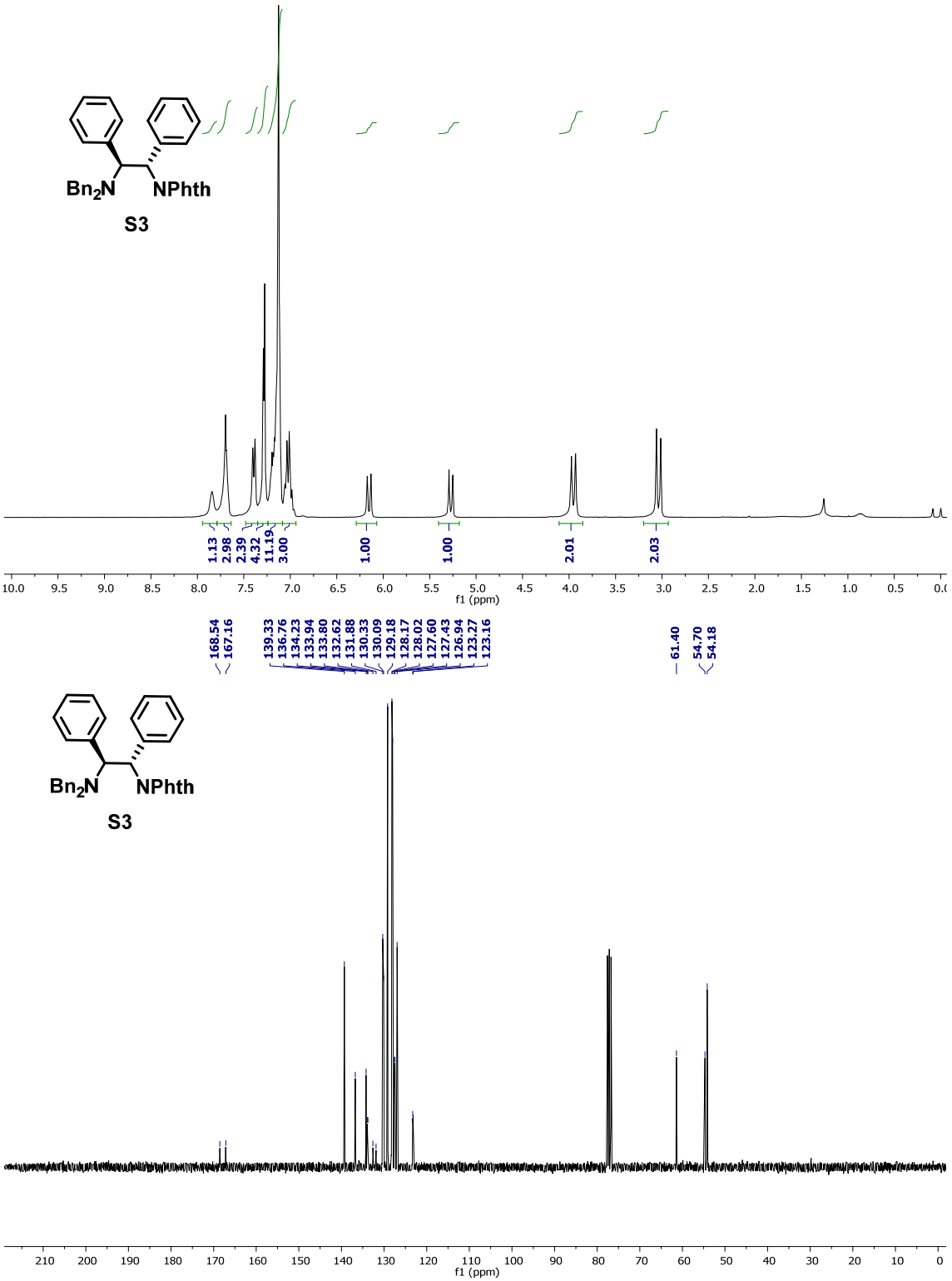


Figure S16: ^{1}H and ^{13}C NMR spectra for compound **S3** (300 and 75 MHz, $CDCl_3$, 298K).

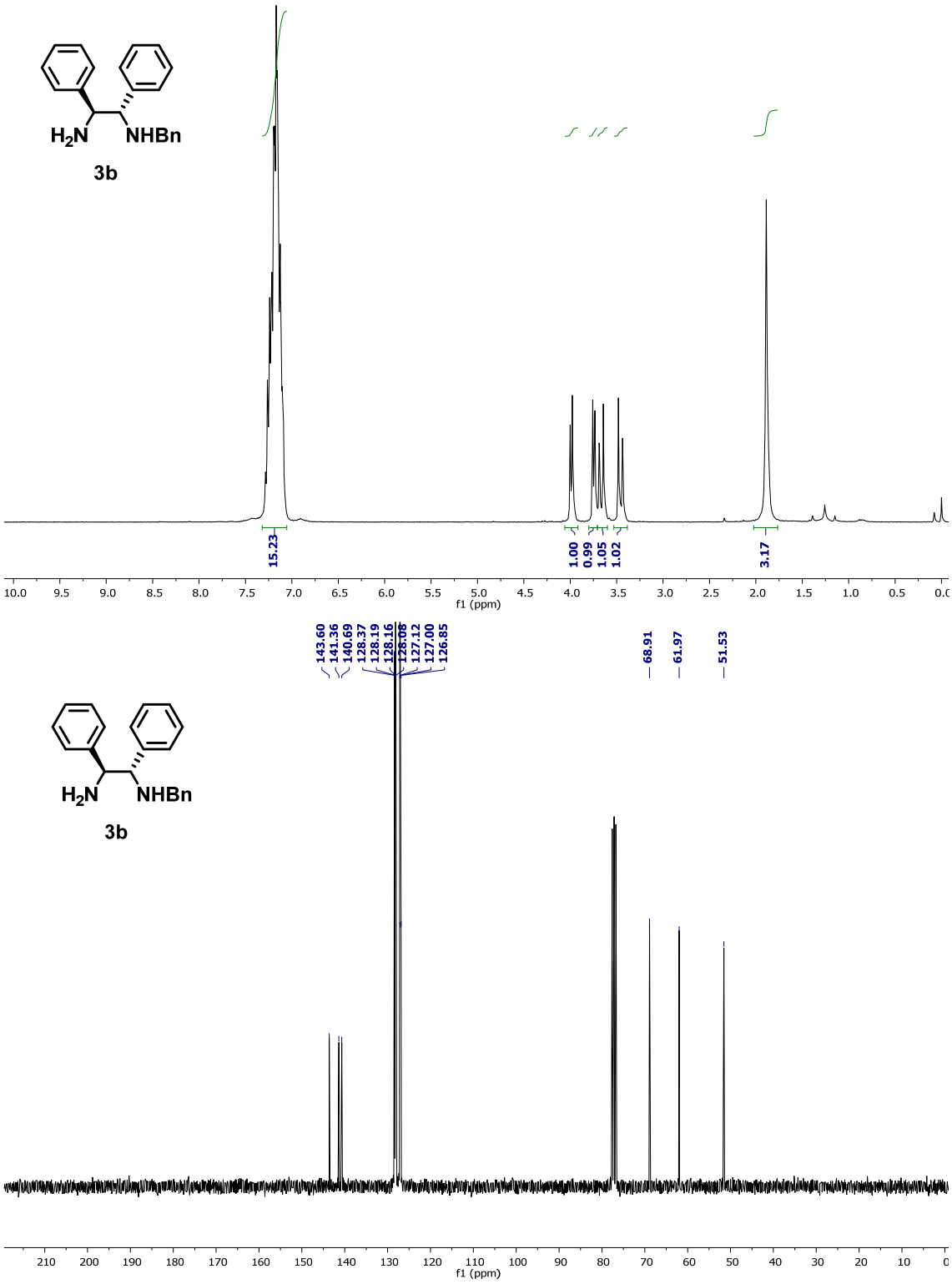


Figure S17: ^{1}H and ^{13}C NMR spectra for compound **3b** (300 and 75 MHz, $CDCl_3$, 298K).

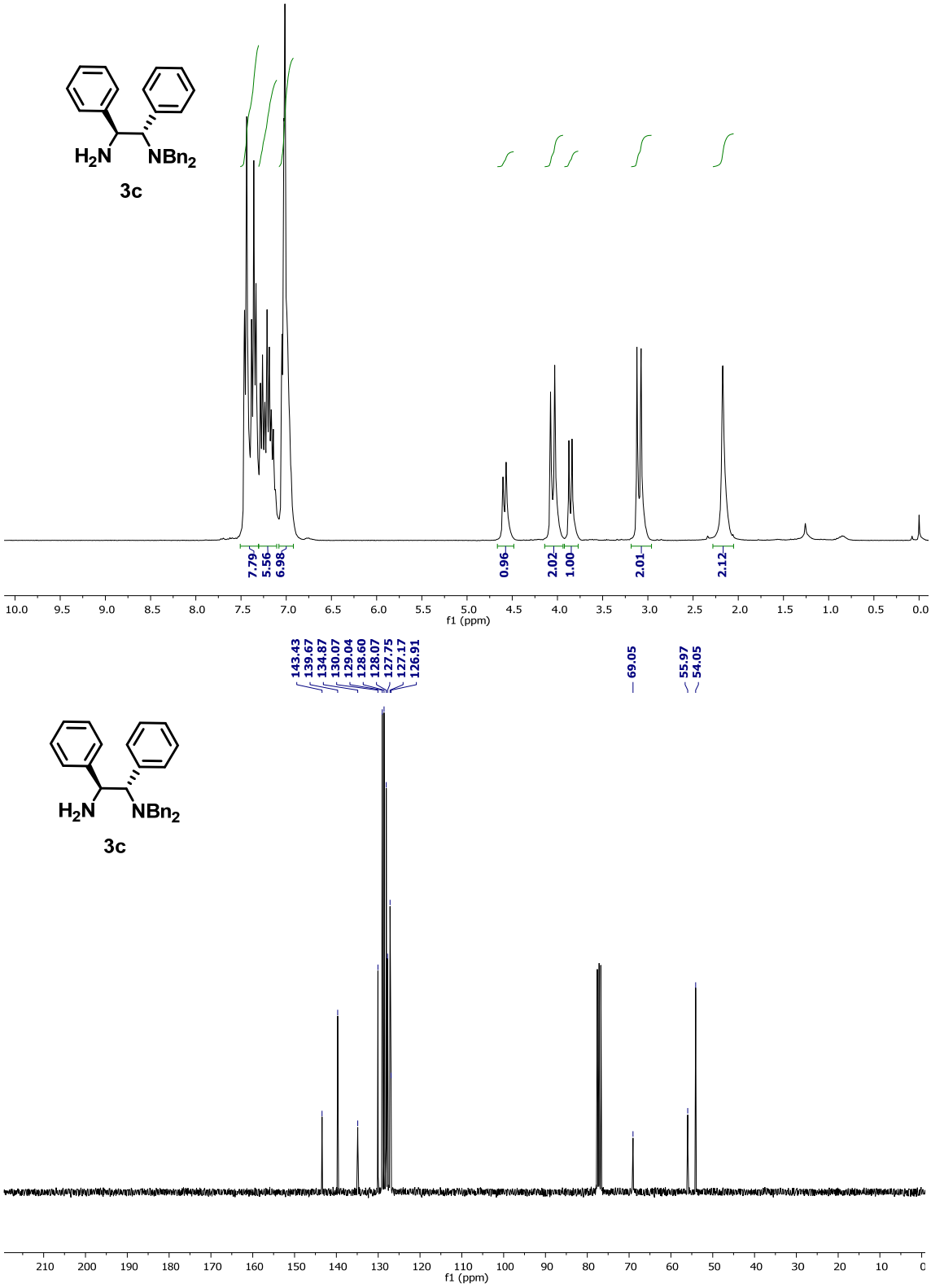


Figure S18: ^{1}H and ^{13}C NMR spectra for compound **3c** (300 and 75 MHz, $CDCl_3$, 298K).

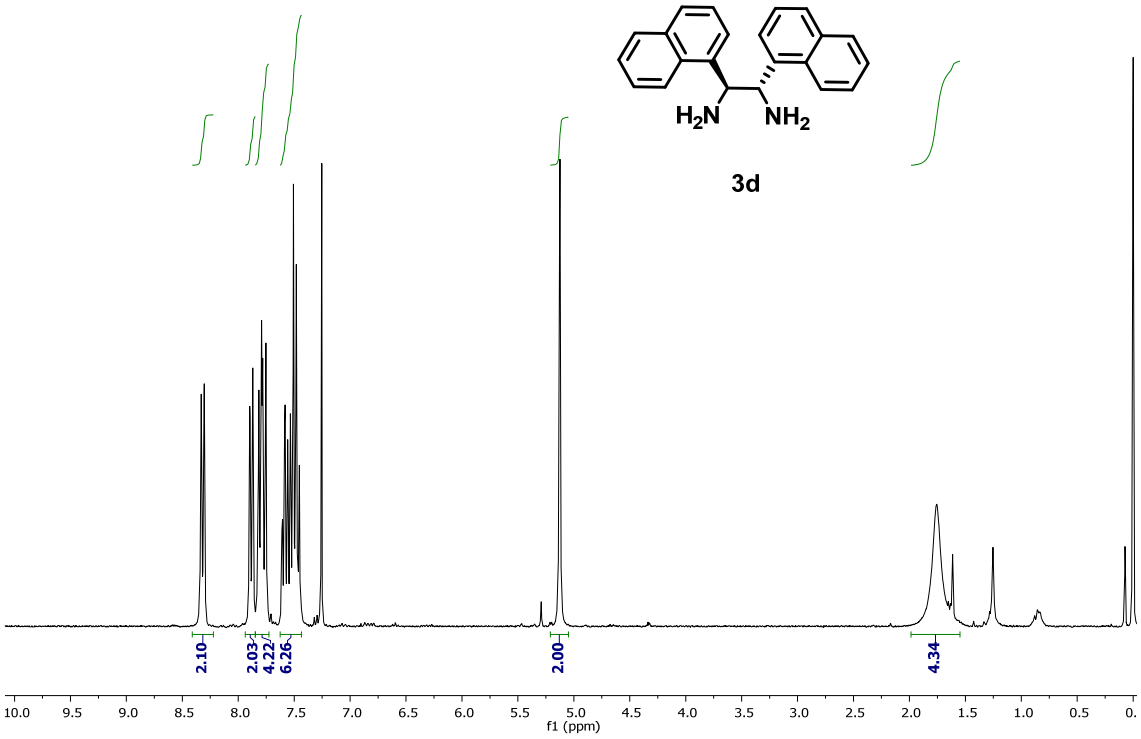


Figure S19: ^{1}H NMR spectrum for compound **3d** (300 MHz, $CDCl_3$, 298K).

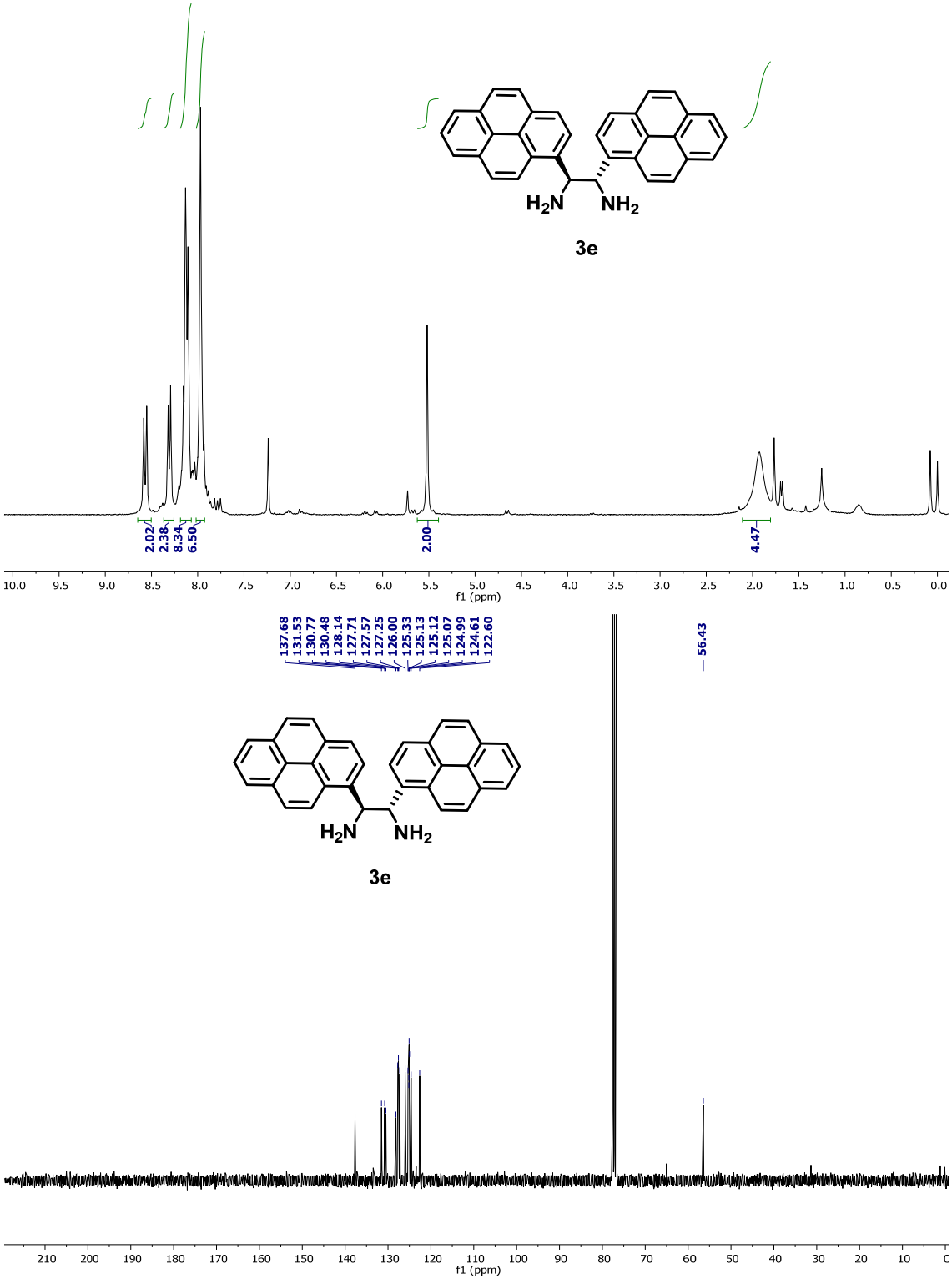


Figure S20: ^{1}H and ^{13}C NMR spectra for compound **3e** (300 and 75 MHz, $CDCl_3$, 298K).

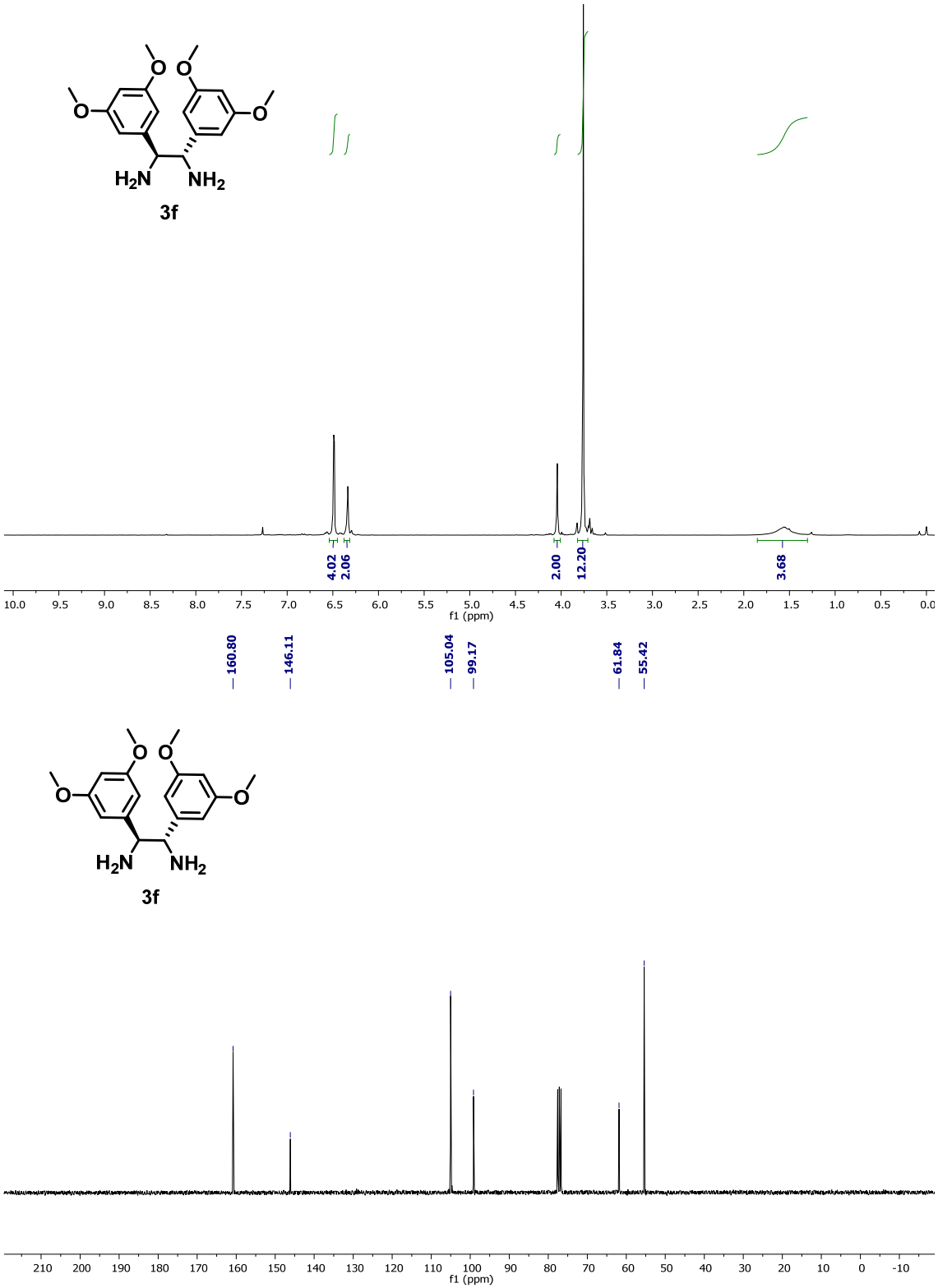


Figure S21: ^{1}H and ^{13}C NMR spectra for compound **3f** (300 and 75 MHz, $CDCl_3$, 298K).

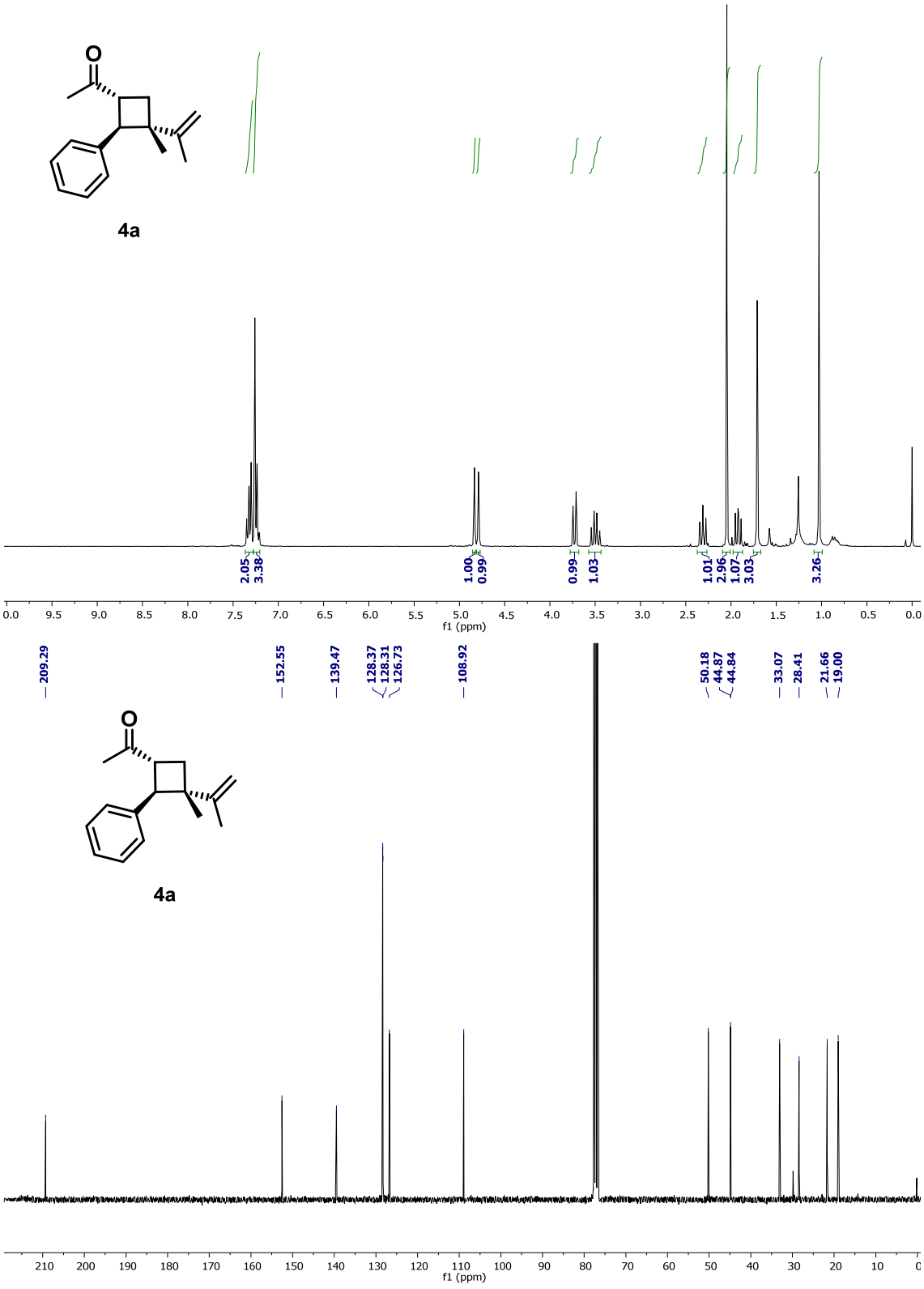


Figure S22: ^{1}H and ^{13}C NMR spectra for compound **4a** (300 and 75 MHz, $CDCl_3$, 298K).

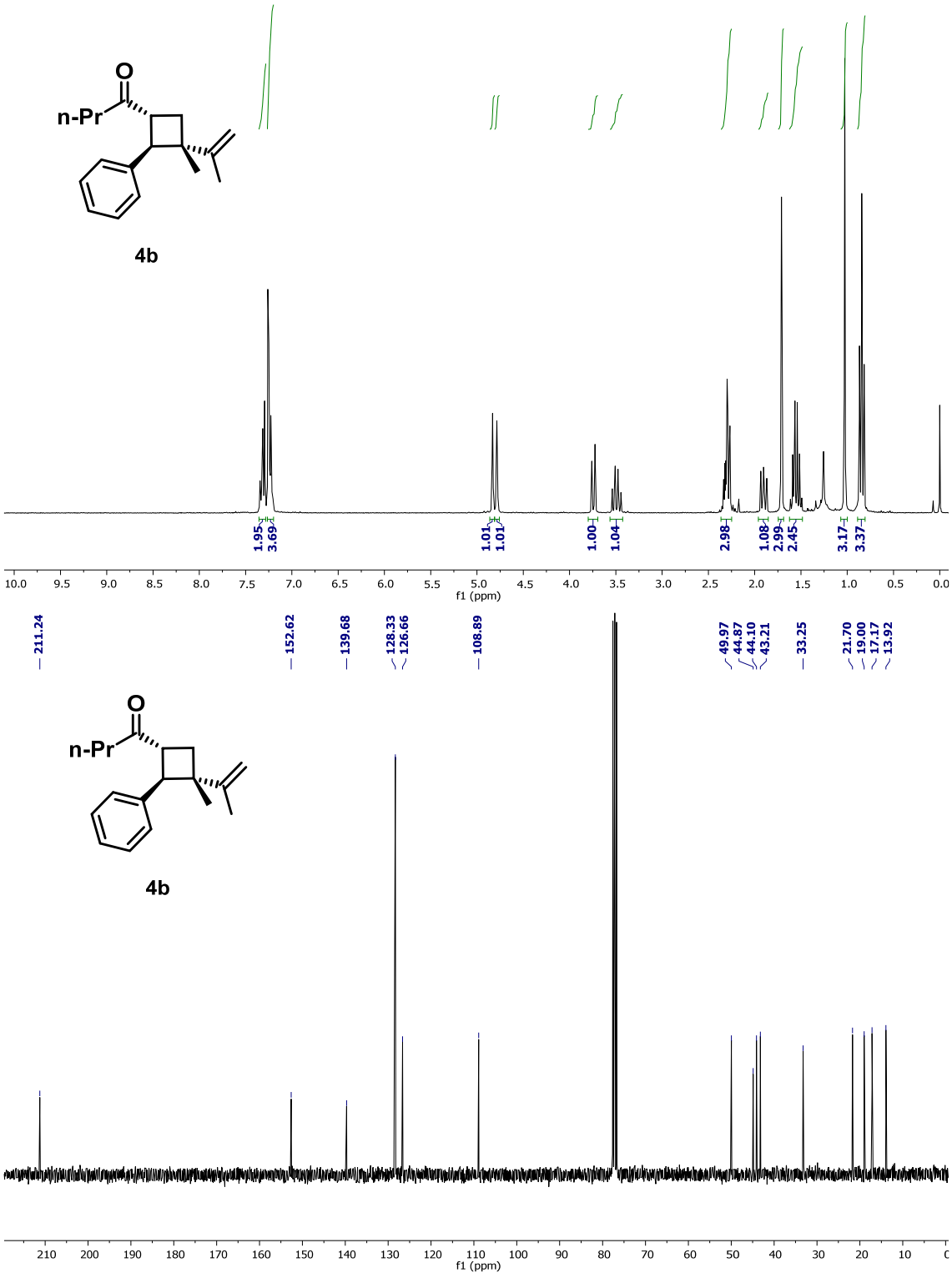


Figure S23: ^{1}H and ^{13}C NMR spectra for compound **4b** (300 and 75 MHz, $CDCl_3$, 298K).

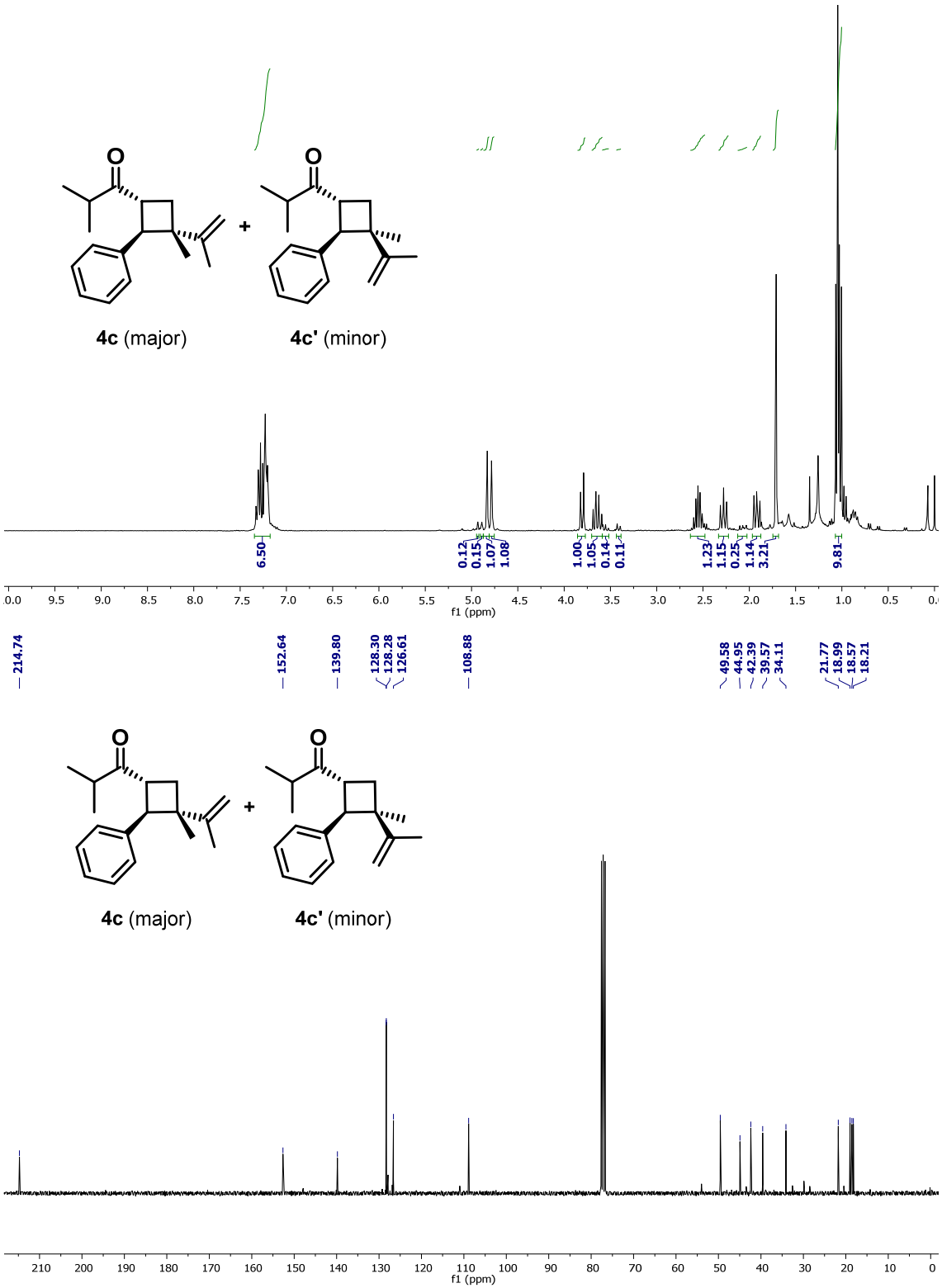


Figure S24: ^{1}H and ^{13}C NMR spectra for compound **4c** (major and minor diastereoisomer; *dr* = 9:1) (300 and 75 MHz, $CDCl_3$, 298K).

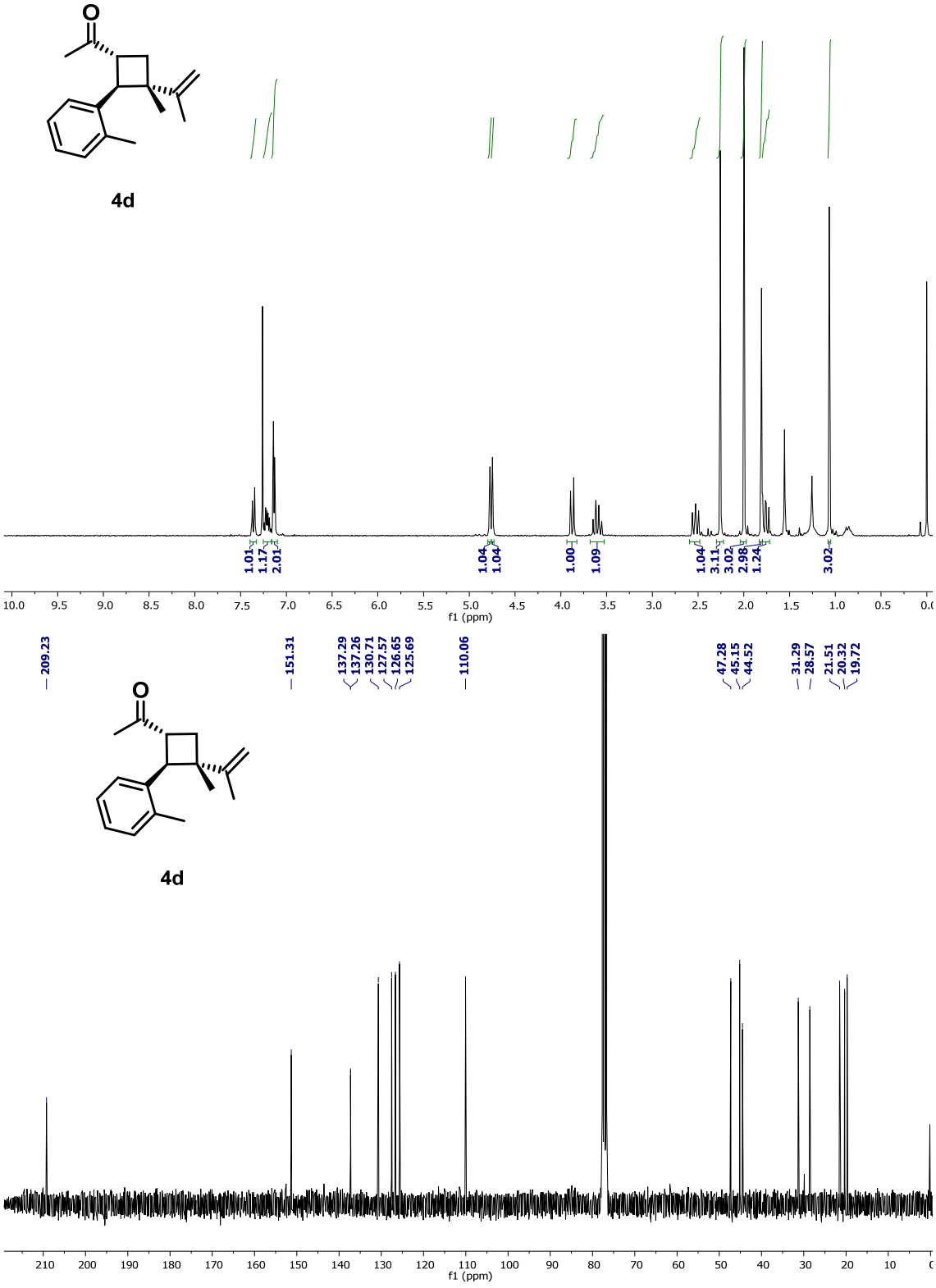


Figure S25: ^{1}H and ^{13}C NMR spectra for compound **4d** (300 and 75 MHz, $CDCl_3$, 298K).

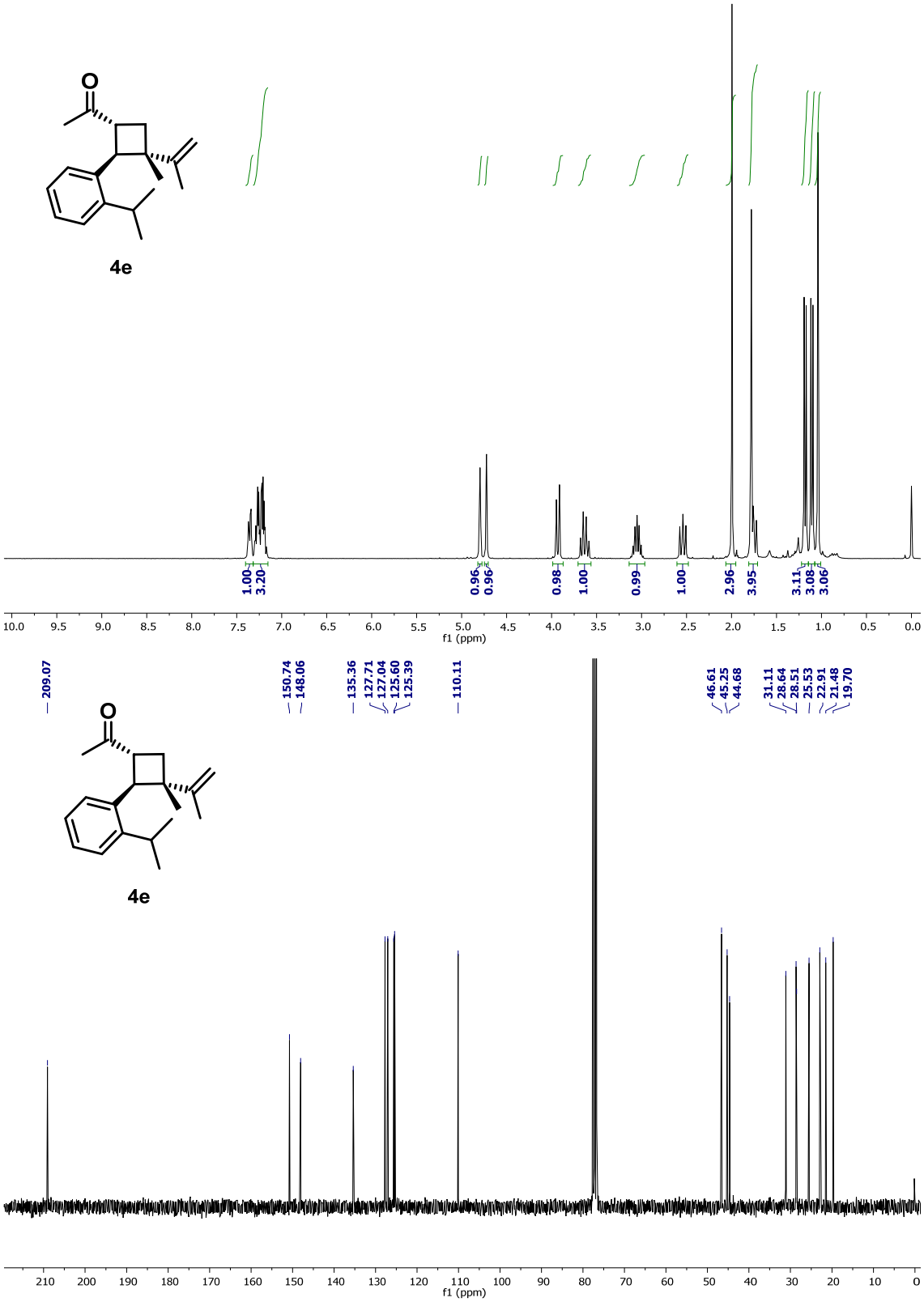


Figure S26: ^{1}H and ^{13}C NMR spectra for compound **4e** (300 and 75 MHz, $CDCl_3$, 298K).

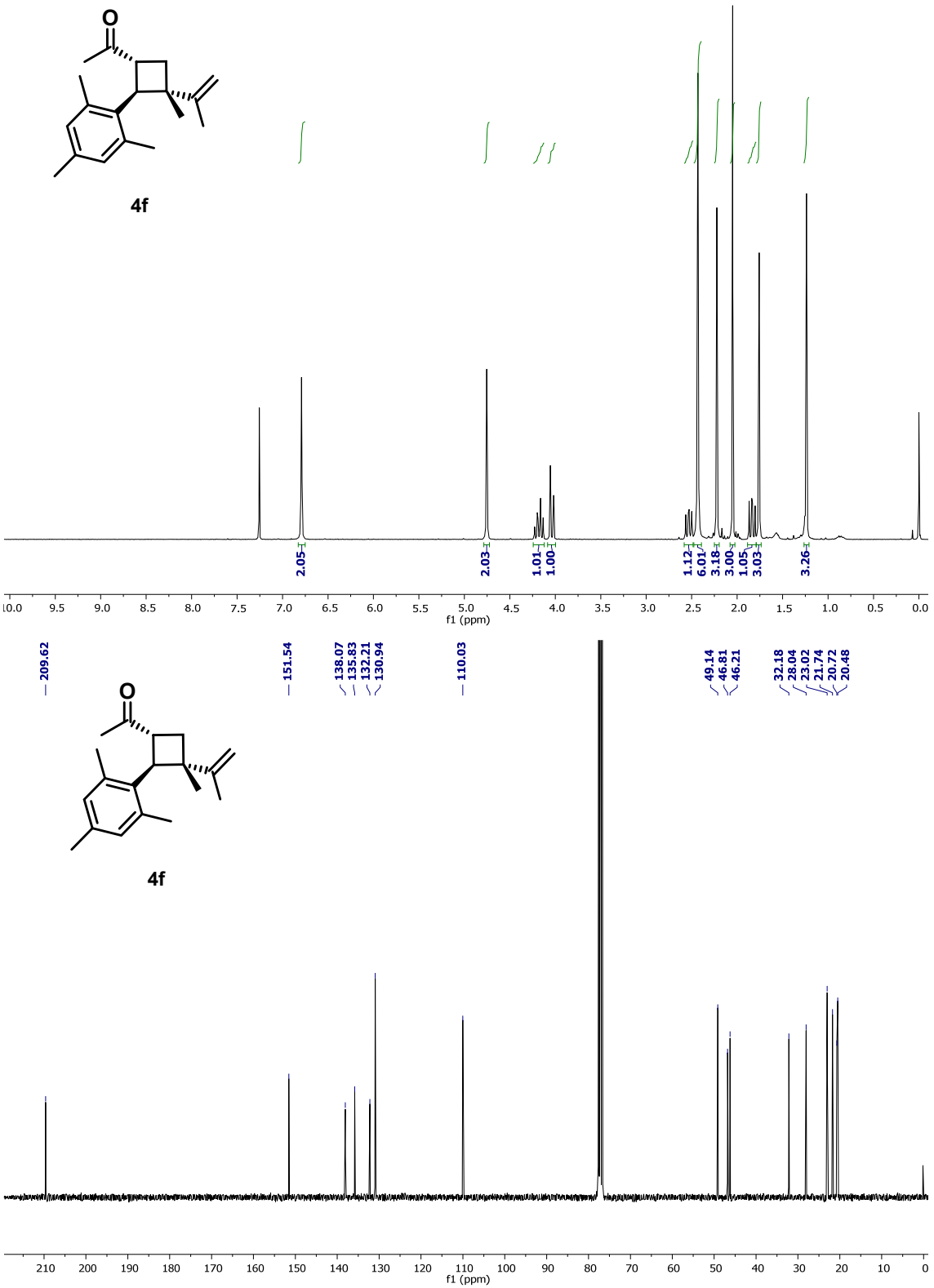


Figure S27: ^{1}H and ^{13}C NMR spectra for compound **4f** (300 and 75 MHz, $CDCl_3$, 298K).

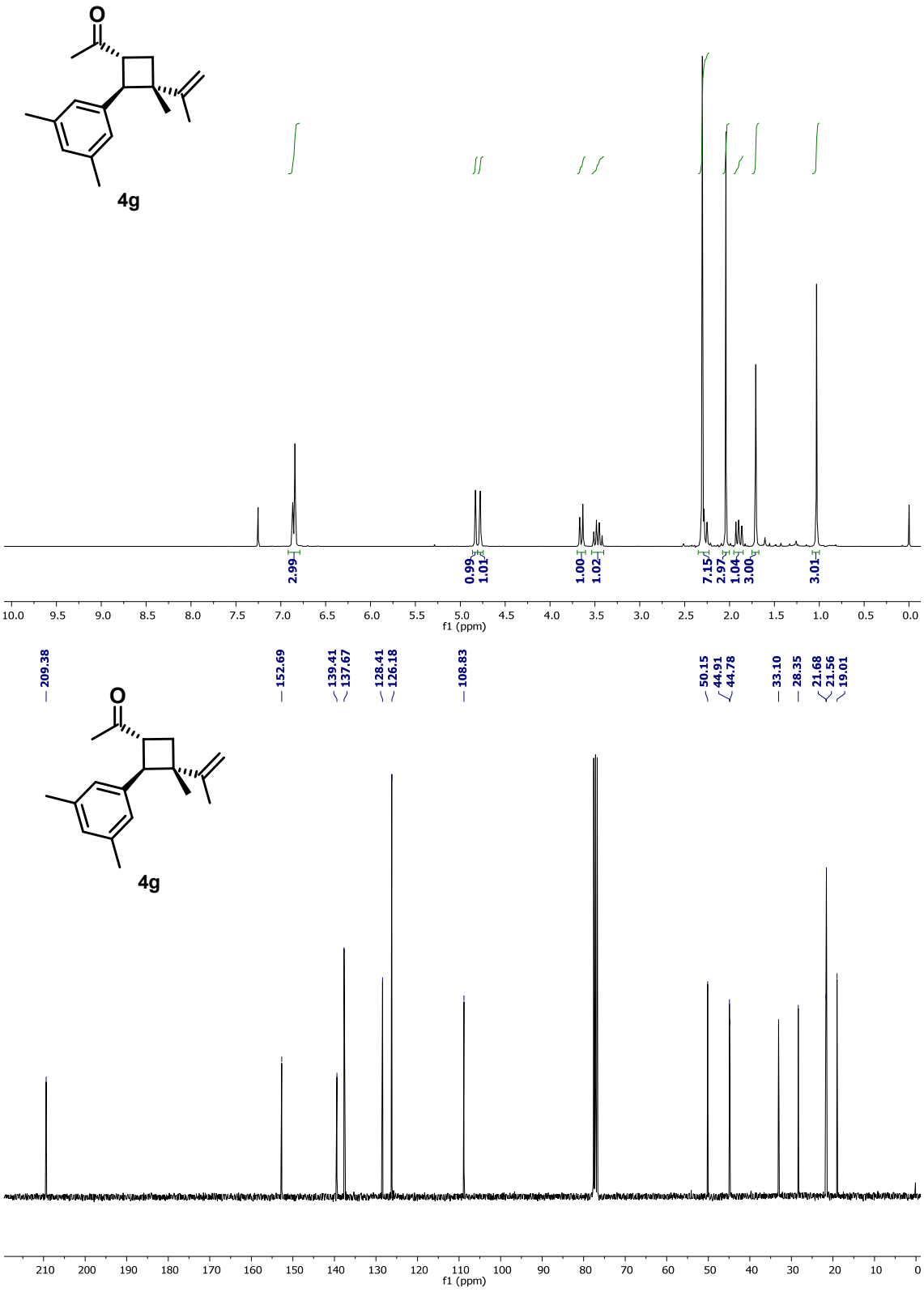


Figure S28: ^{1}H and ^{13}C NMR spectra for compound **4g** (300 and 75 MHz, $CDCl_3$, 298K).

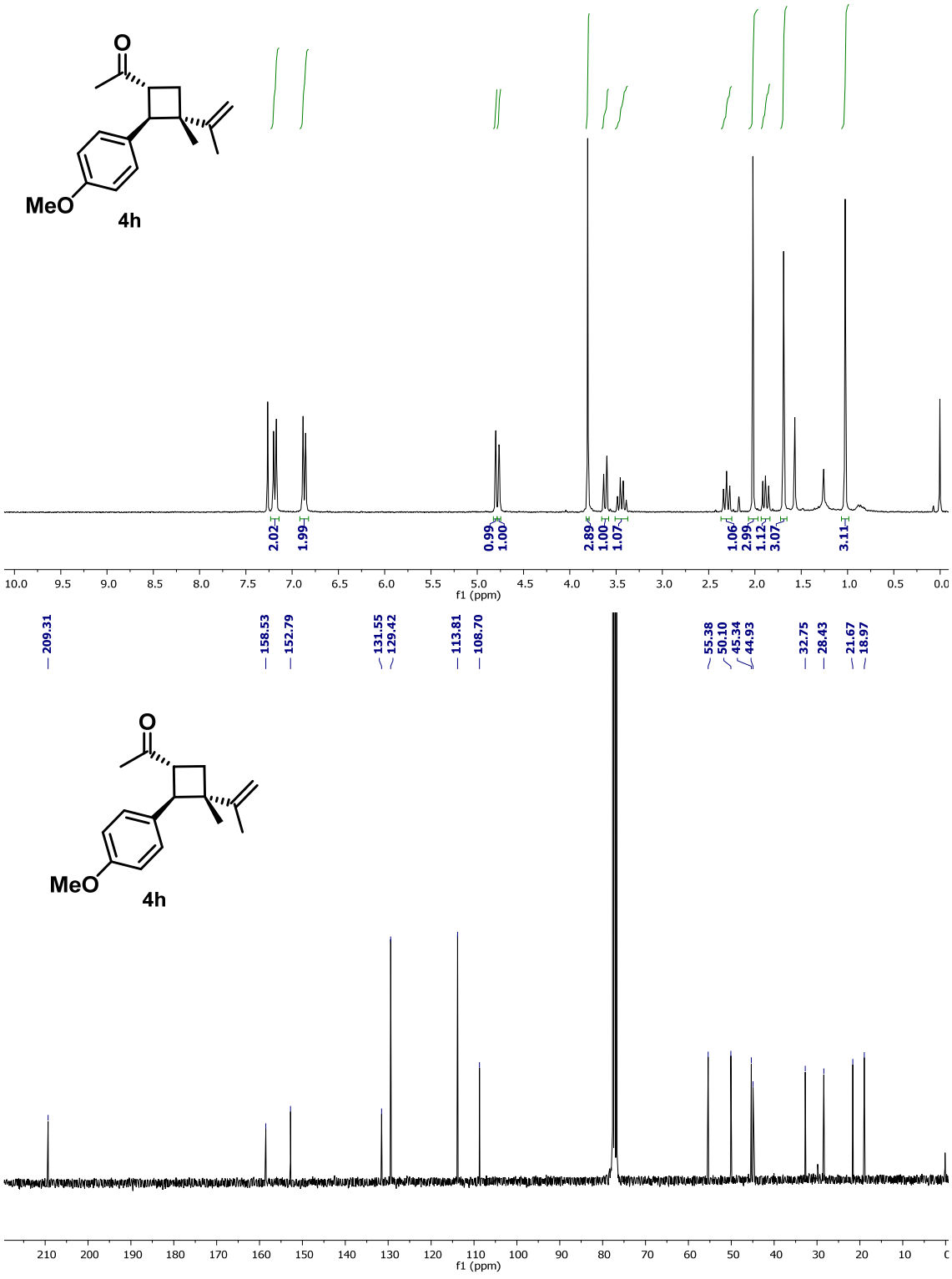


Figure S29: ^{1}H and ^{13}C NMR spectra for compound **4h** (300 and 75 MHz, $CDCl_3$, 298K).

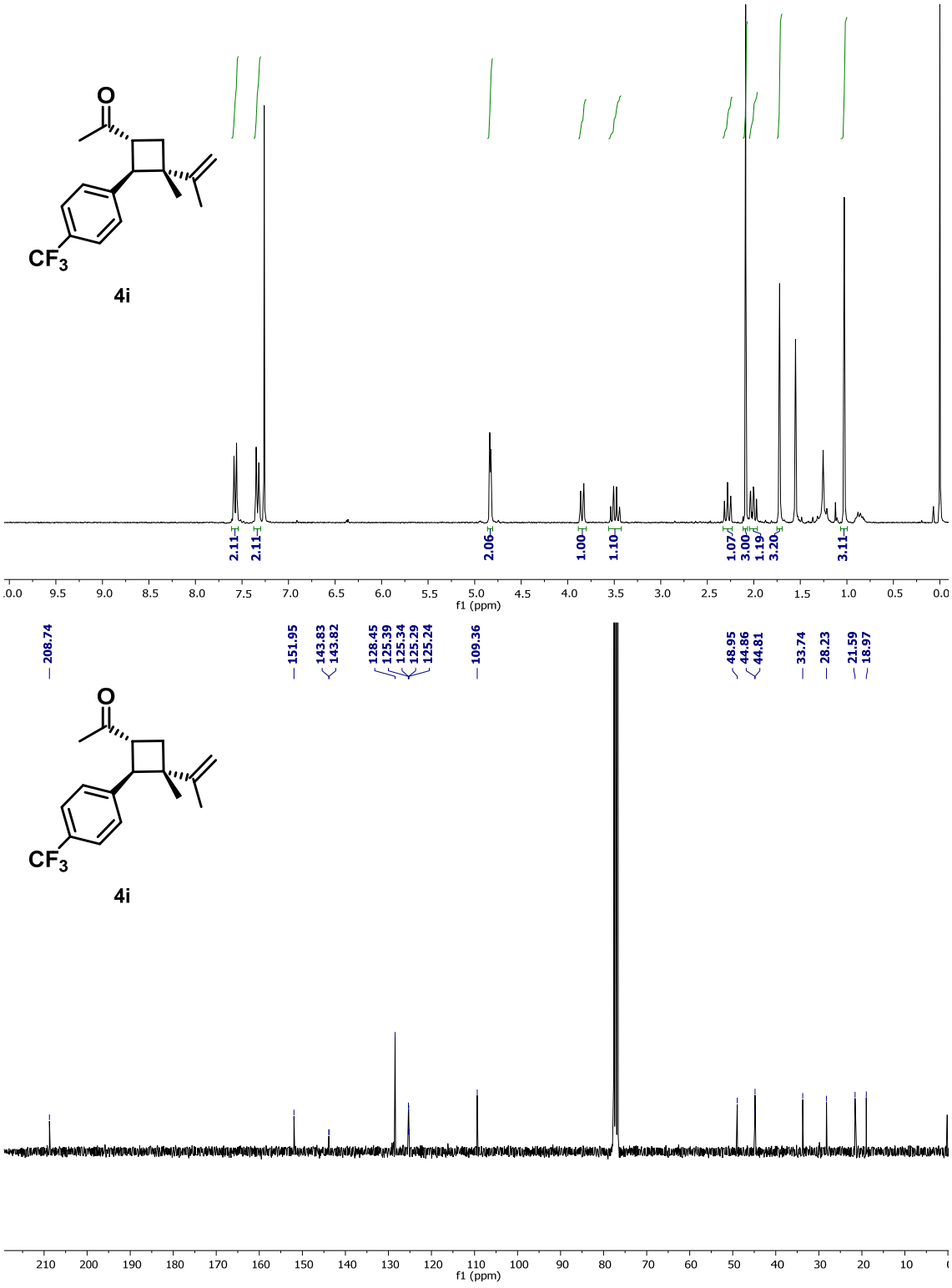


Figure S30: ^{1}H and ^{13}C NMR spectra for compound **4i** (300 and 75 MHz, $CDCl_3$, 298K).

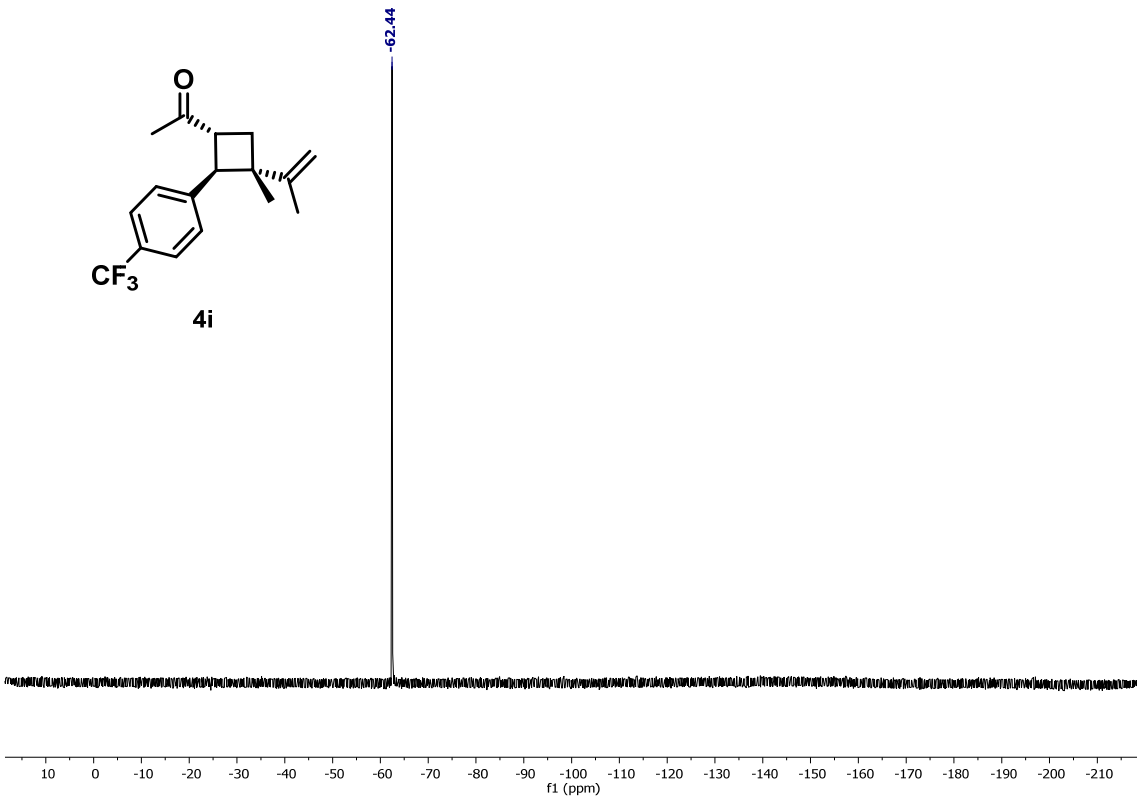


Figure S31: ^{19}F NMR spectrum for compound **4i** (282 MHz, $CDCl_3$, 298K).

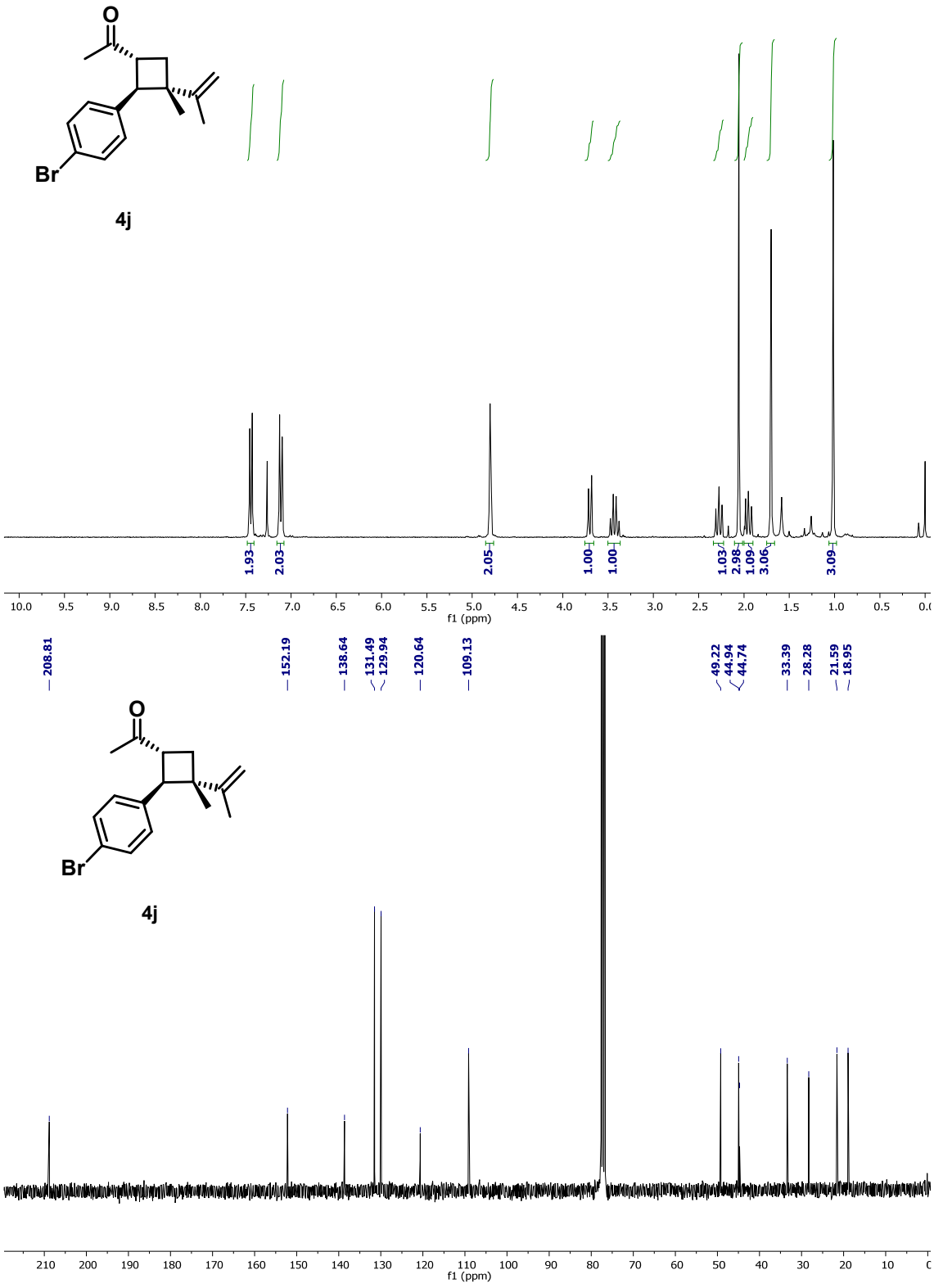


Figure S32: ^{1}H and ^{13}C NMR spectra for compound **4j** (300 and 75 MHz, $CDCl_3$, 298K).

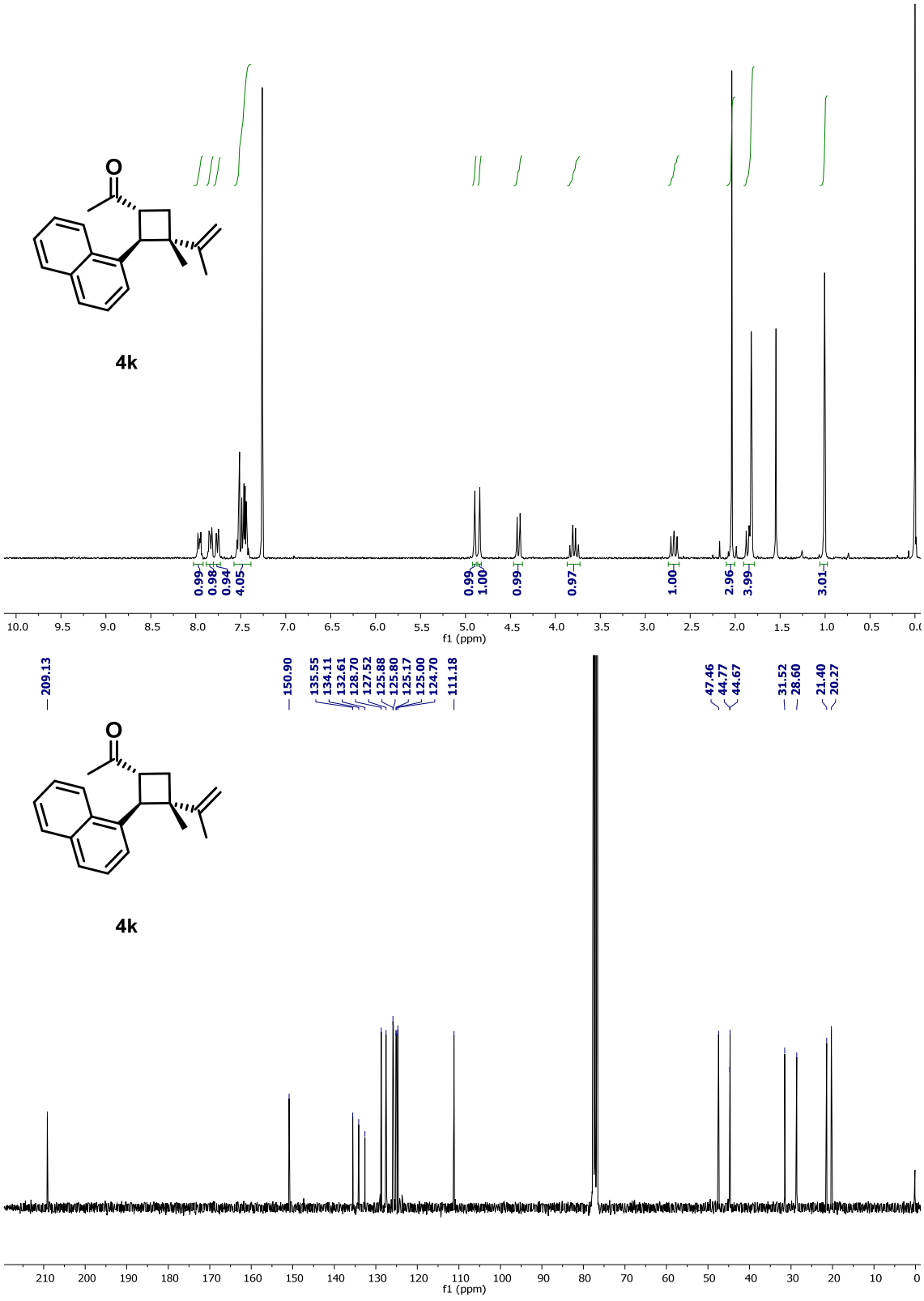


Figure S33: ^{1}H and ^{13}C NMR spectra for compound **4k** (300 and 75 MHz, $CDCl_3$, 298K).

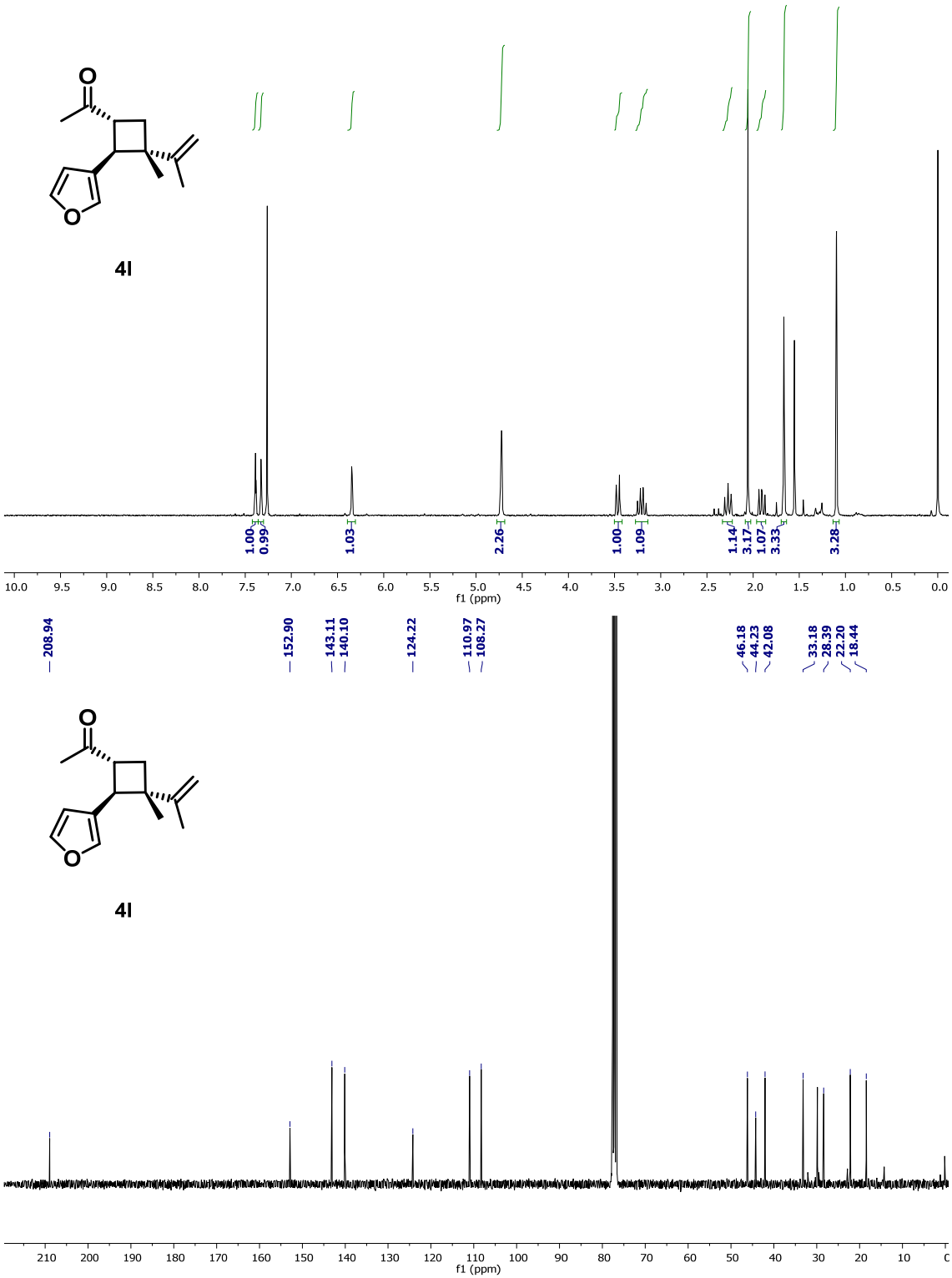


Figure S34: ^{1}H and ^{13}C NMR spectra for compound **4l** (300 and 75 MHz, $CDCl_3$, 298K).

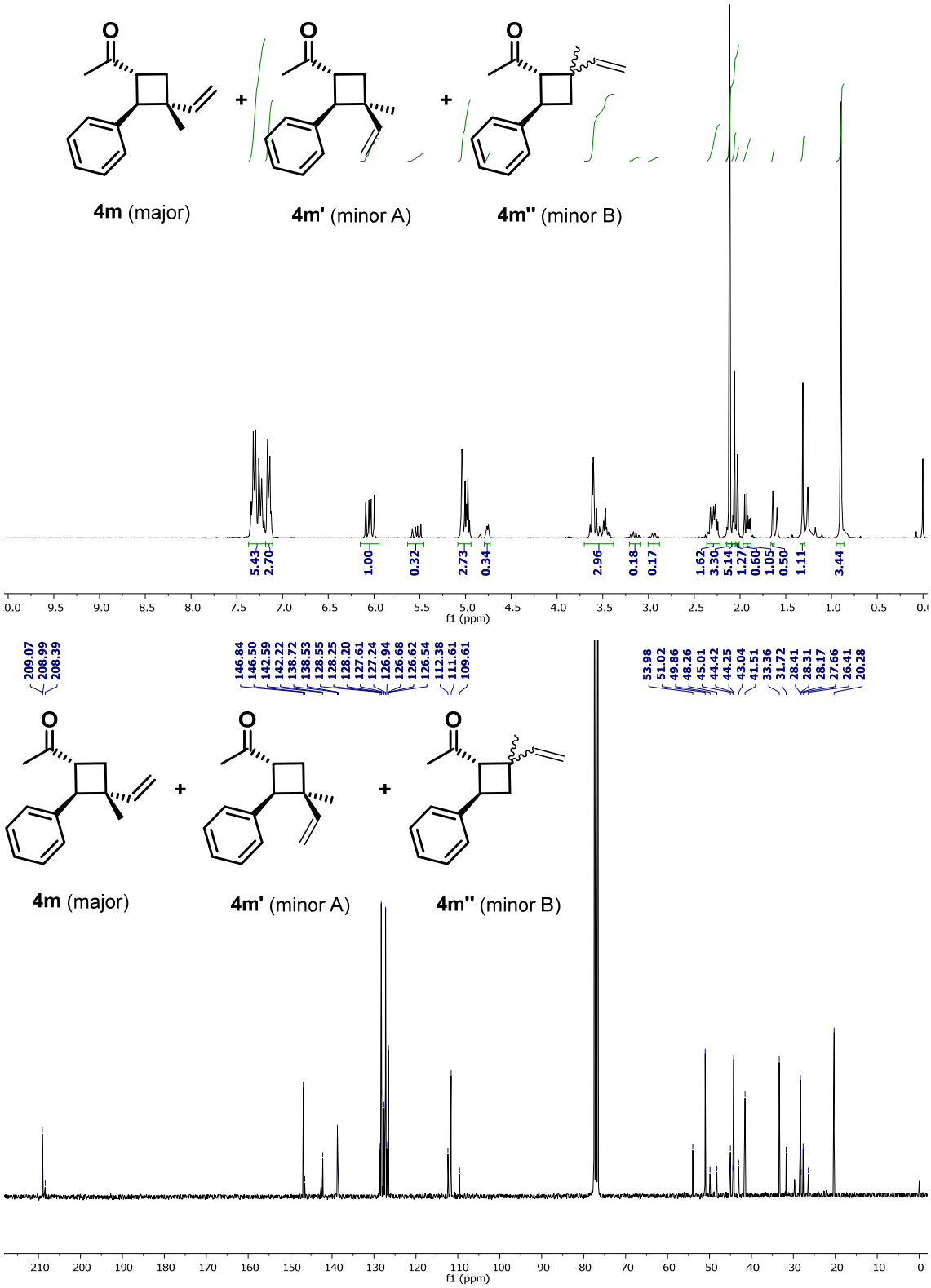


Figure S35: ^{1}H and ^{13}C NMR spectra for compound **4m** (major and minor diastereoisomer; *dr* = 6:2:1) (300 and 75 MHz, $CDCl_3$, 298K).

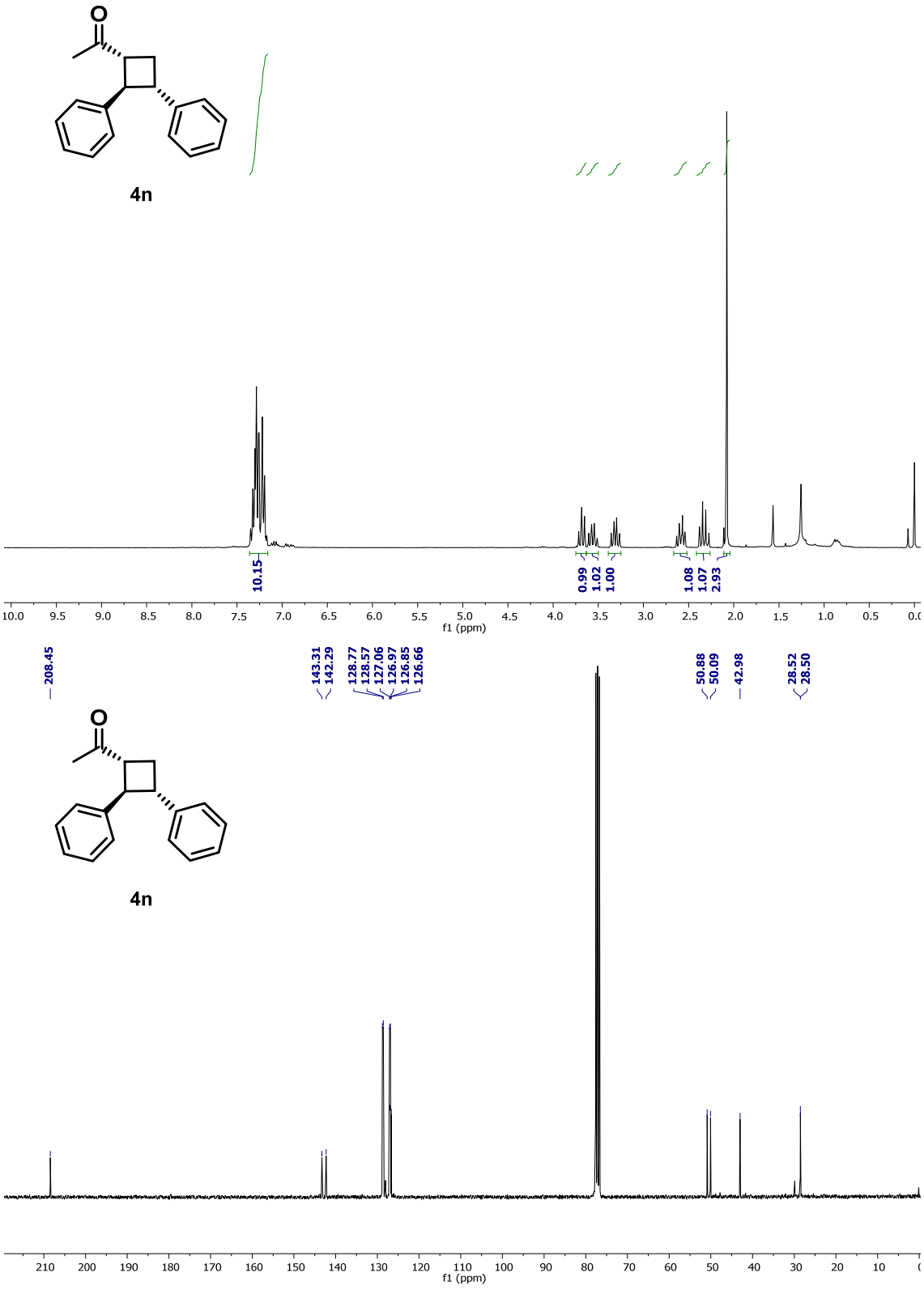


Figure S36: ^{1}H and ^{13}C NMR spectra for compound **4n** (300 and 75 MHz, $CDCl_3$, 298K).

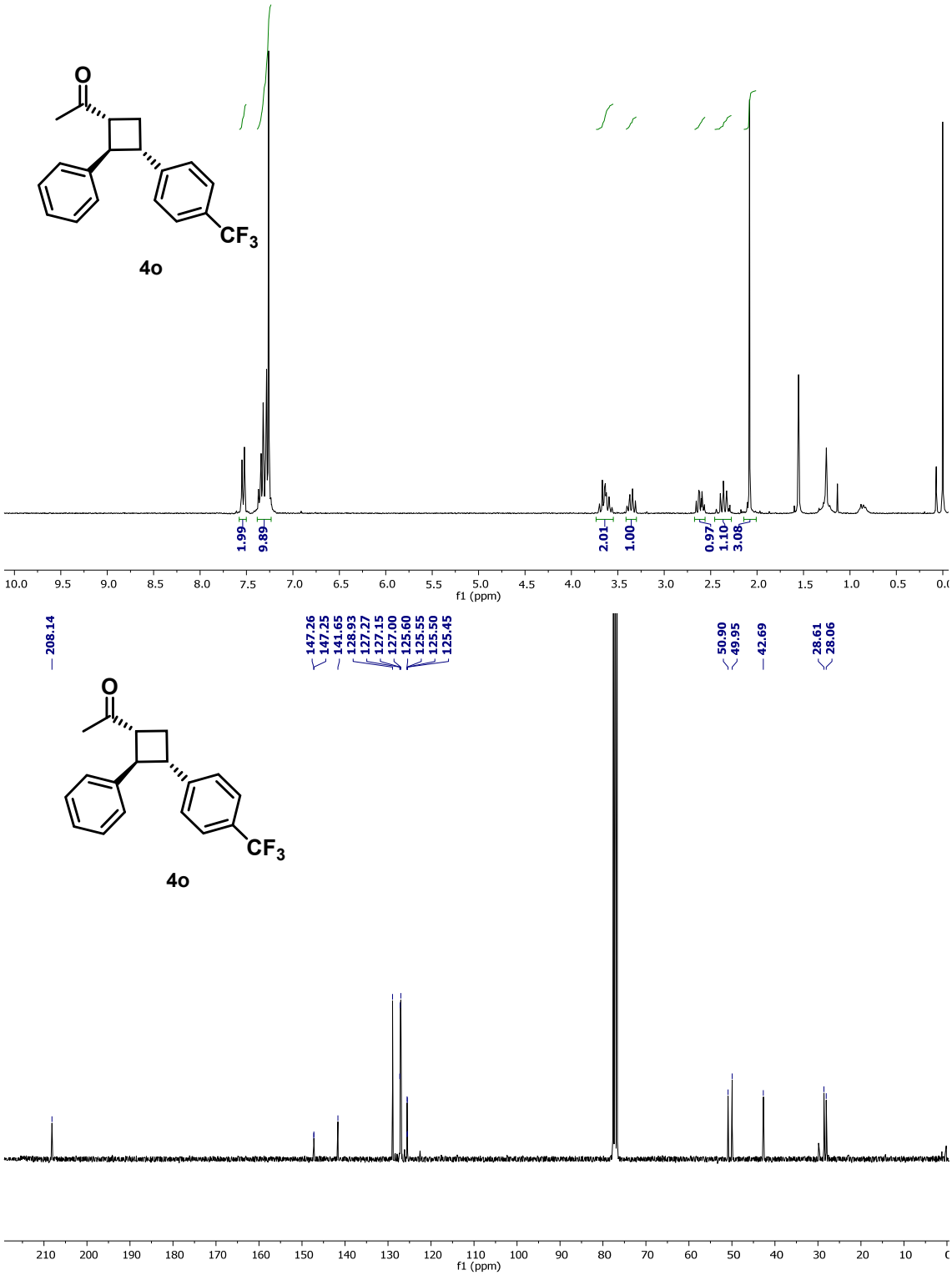


Figure S37: ^{1}H and ^{13}C NMR spectra for compound **4o** (300 and 75 MHz, $CDCl_3$, 298K).

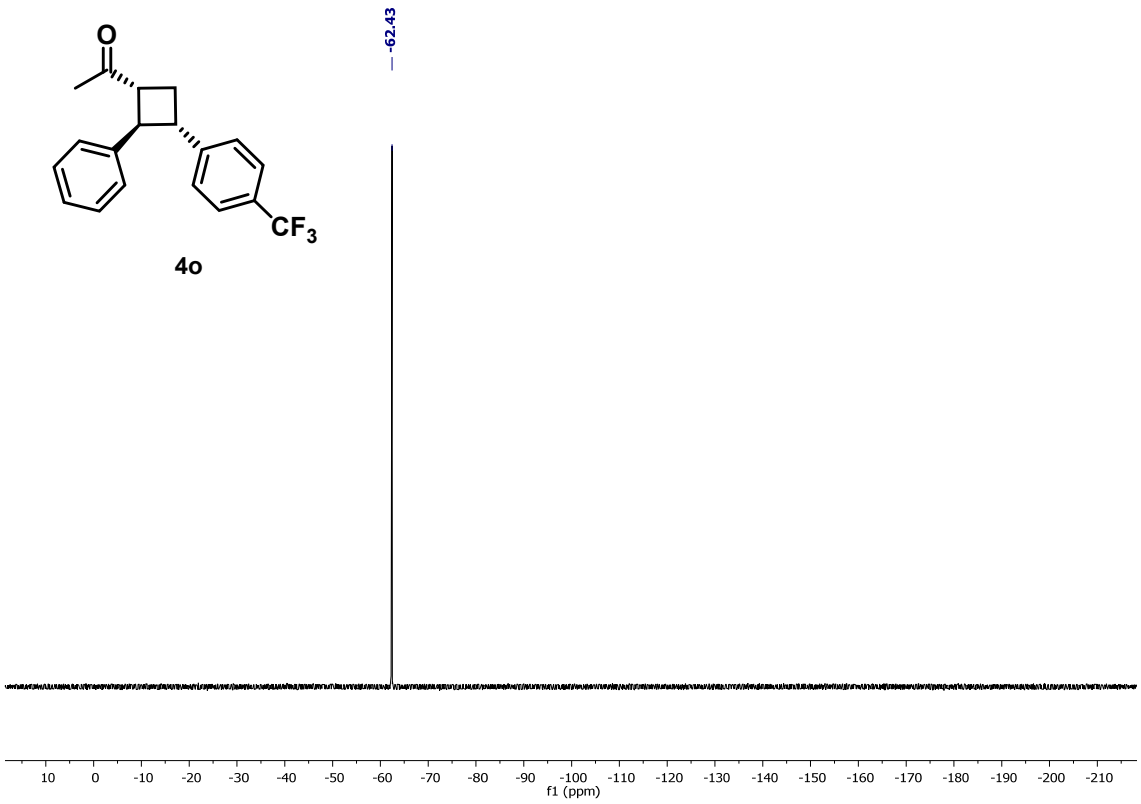


Figure S38: ^{19}F NMR spectrum for compound **4o** (282 MHz, $CDCl_3$, 298K).

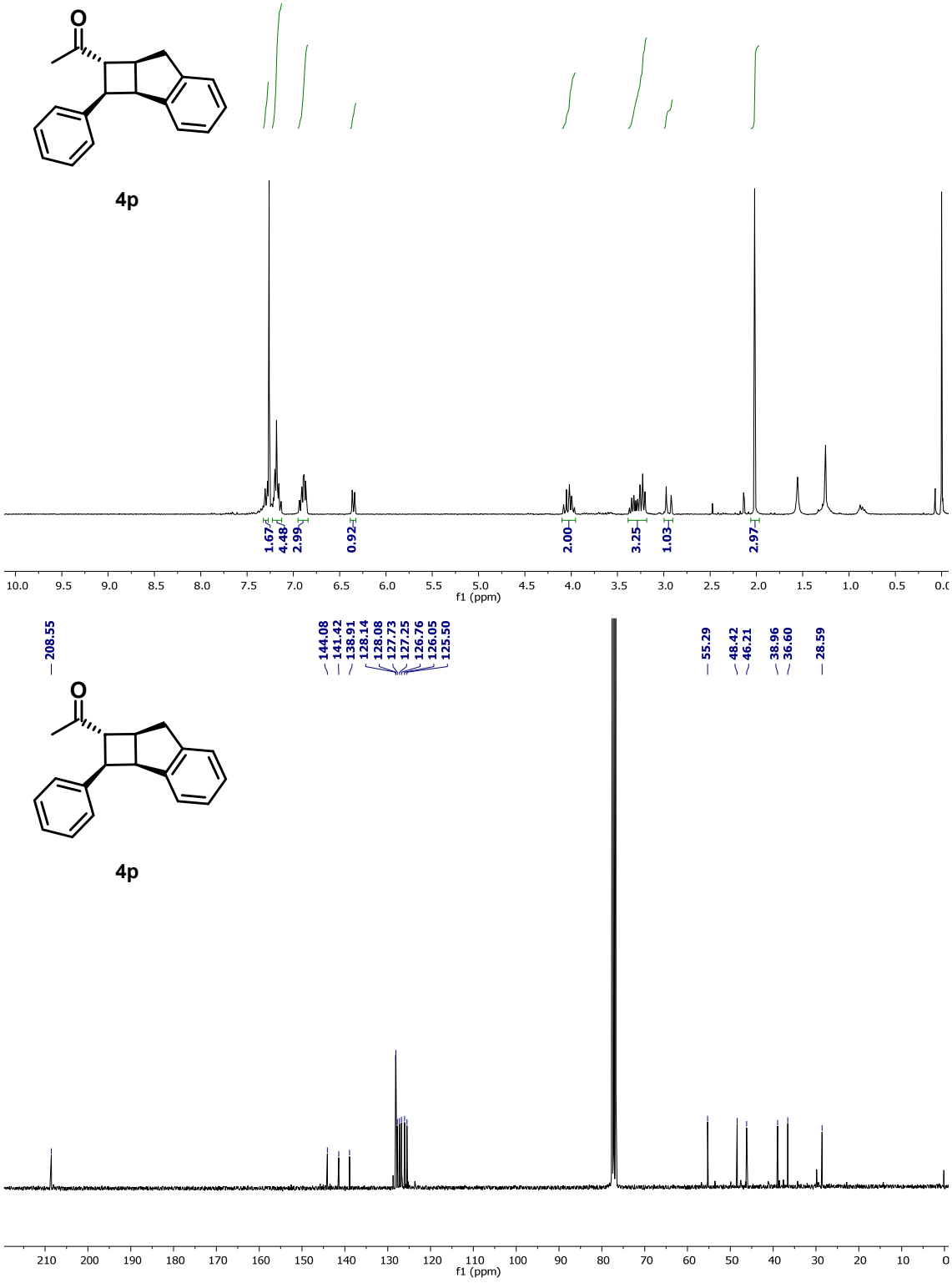


Figure S39: ^{1}H and ^{13}C NMR spectra for compound **4p** (300 and 75 MHz, $CDCl_3$, 298K).

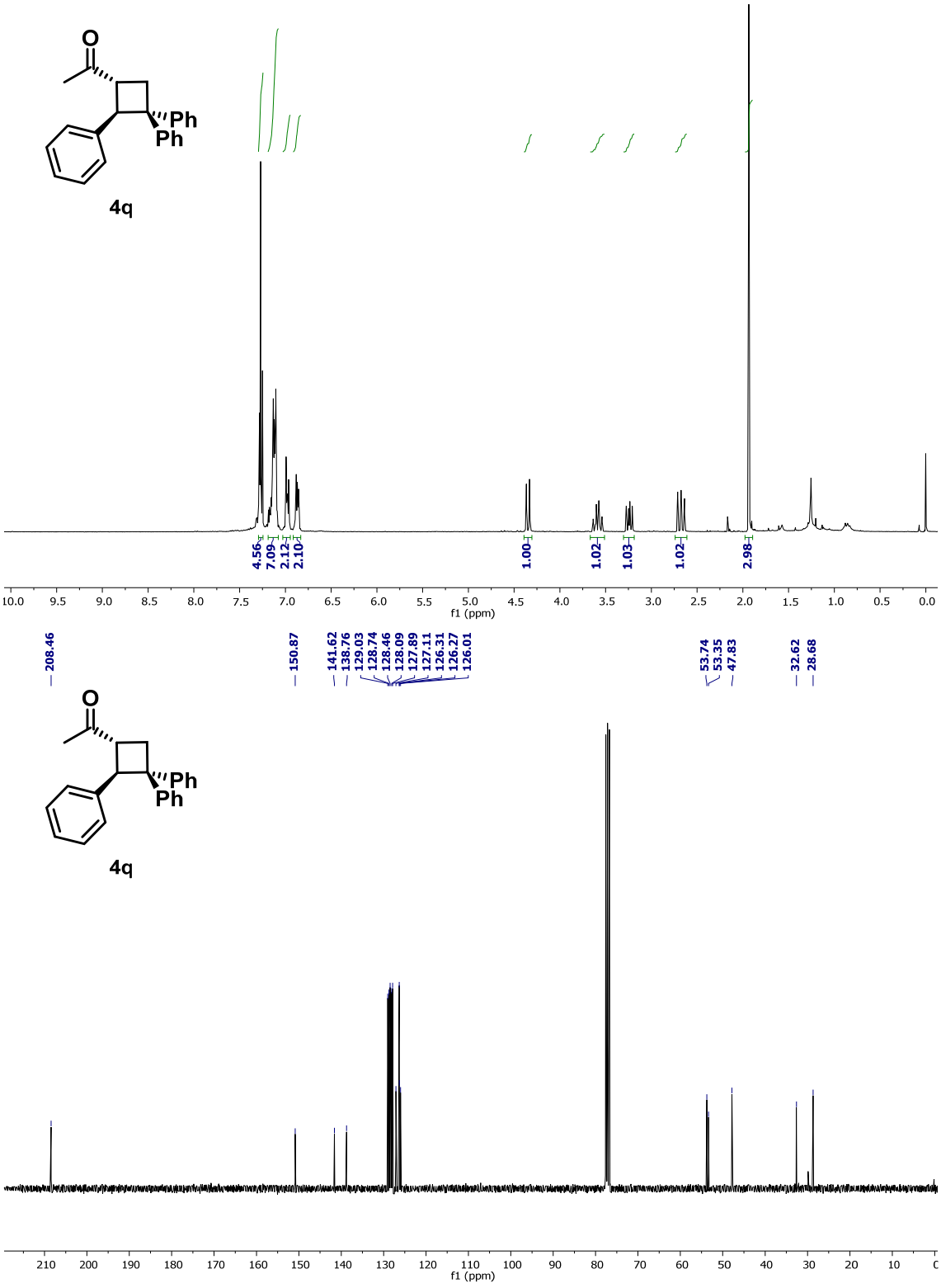


Figure S40: ^{1}H and ^{13}C NMR spectra for compound **4q** (300 and 75 MHz, $CDCl_3$, 298K).

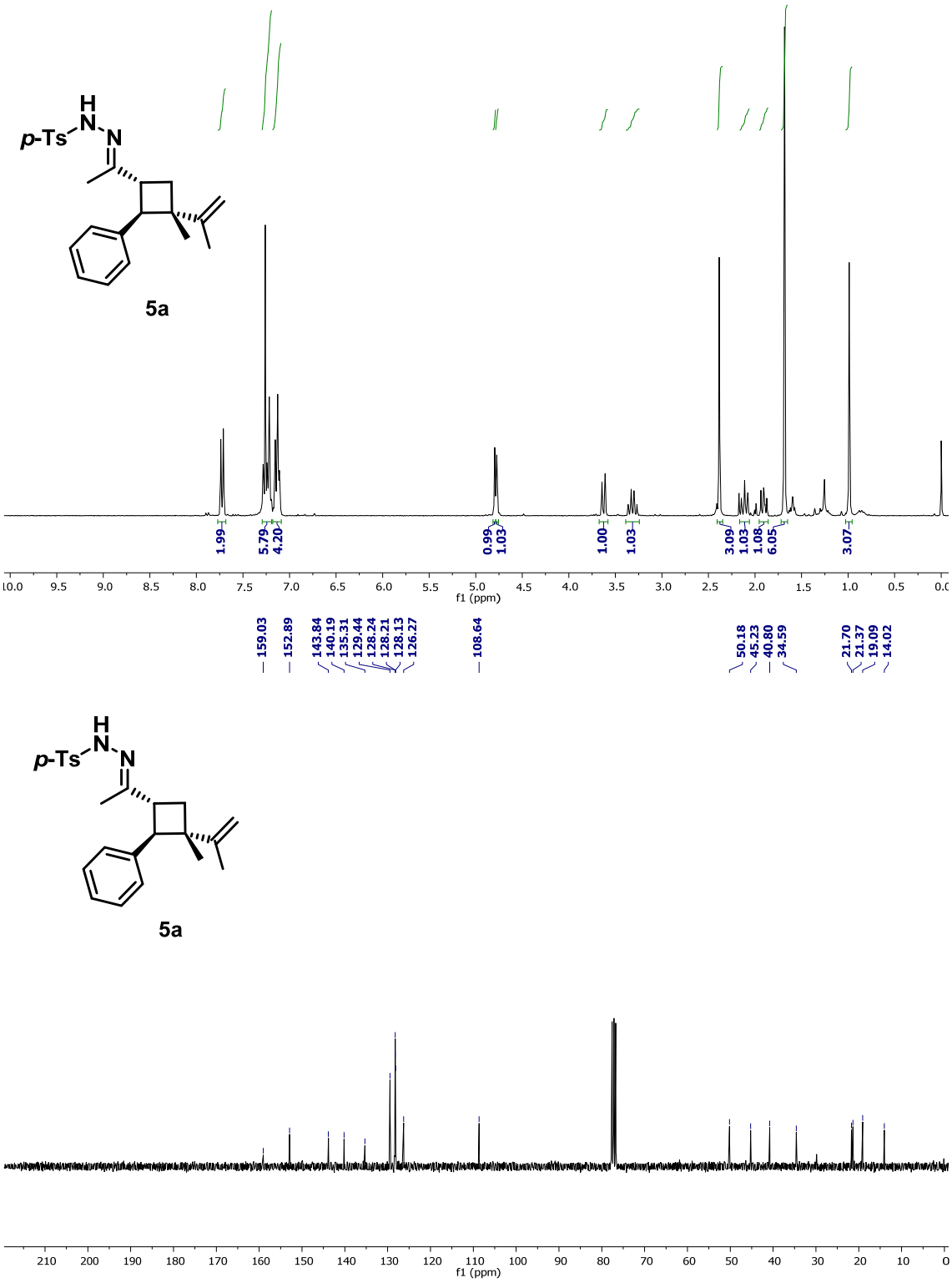


Figure S41: ^{1}H and ^{13}C NMR spectra for compound **5a** (300 and 75 MHz, $CDCl_3$, 298K).

7. Stereochemical Assignment of the Major Diastereoisomer of 4n and 4p

The stereochemical assignment of the relative stereochemistry for **4n** and **4p** was determined by 1D selective NOE experiments.

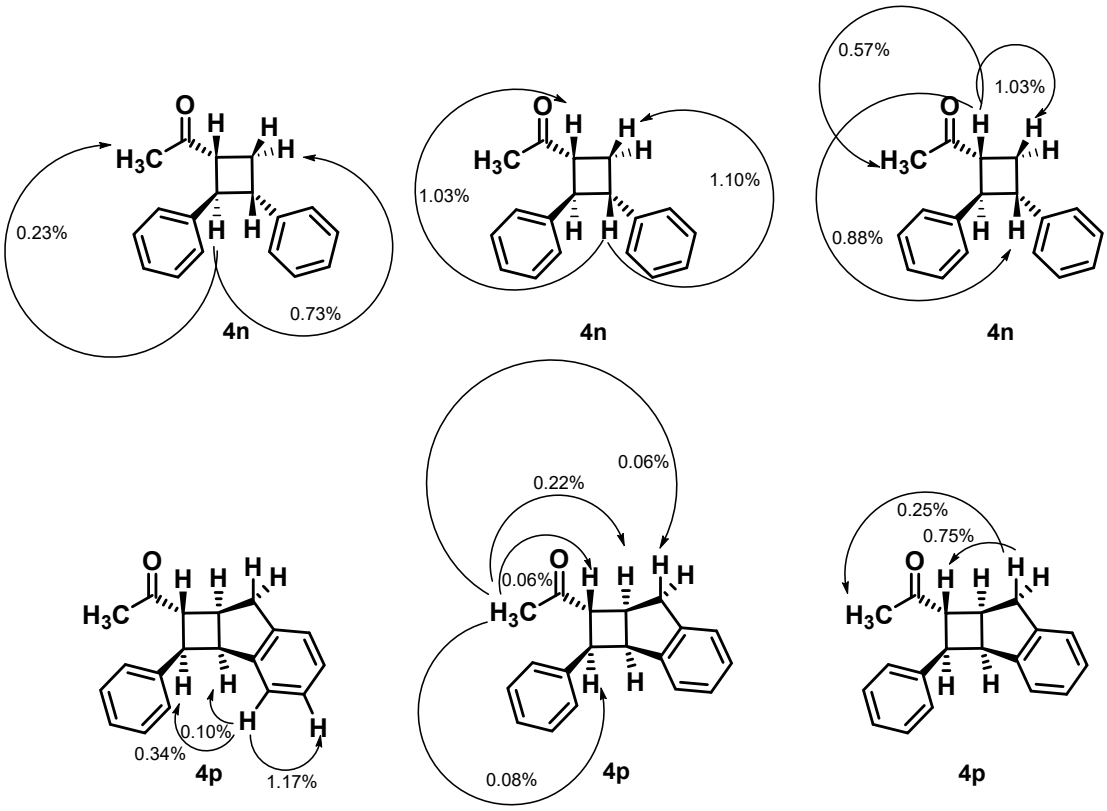


Figure S42: Stereochemical Assignment of the Major Diastereoisomer of **4n** and **4p**.

8. SFC Traces

Determination of the enantiomeric ratio for the enantioenriched cyclobutanes 4.

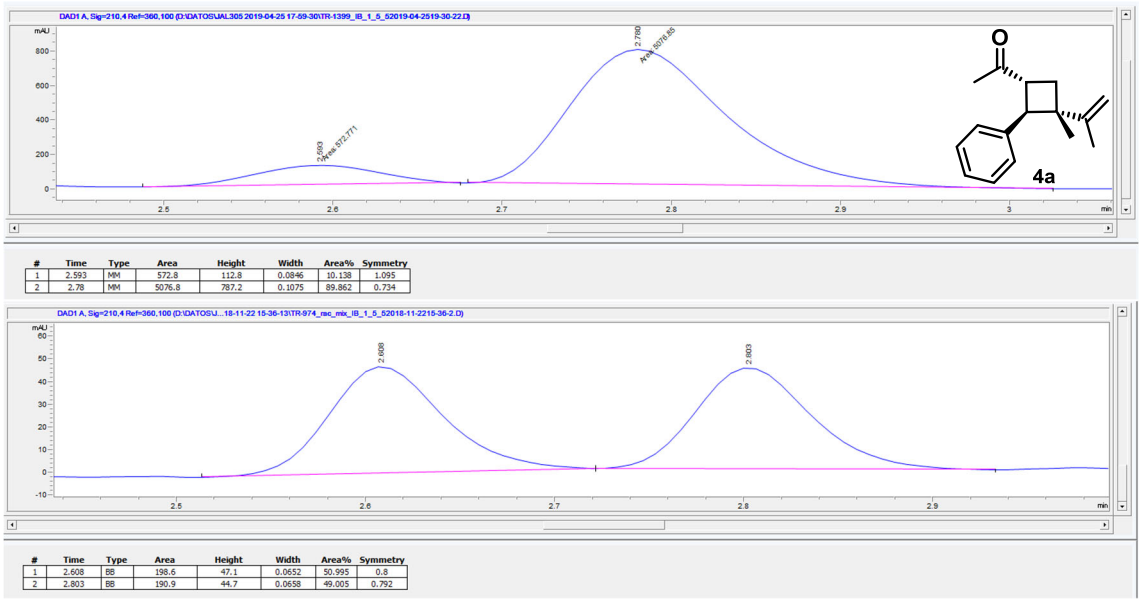


Figure S43: SFC chromatograms for compound **4a** (enantioenriched and racemic samples).

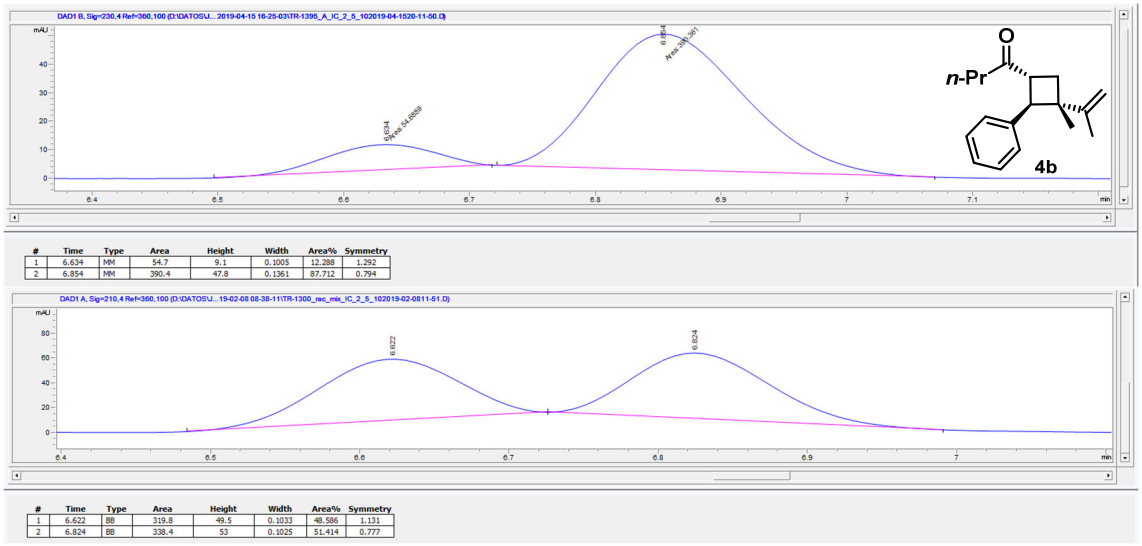
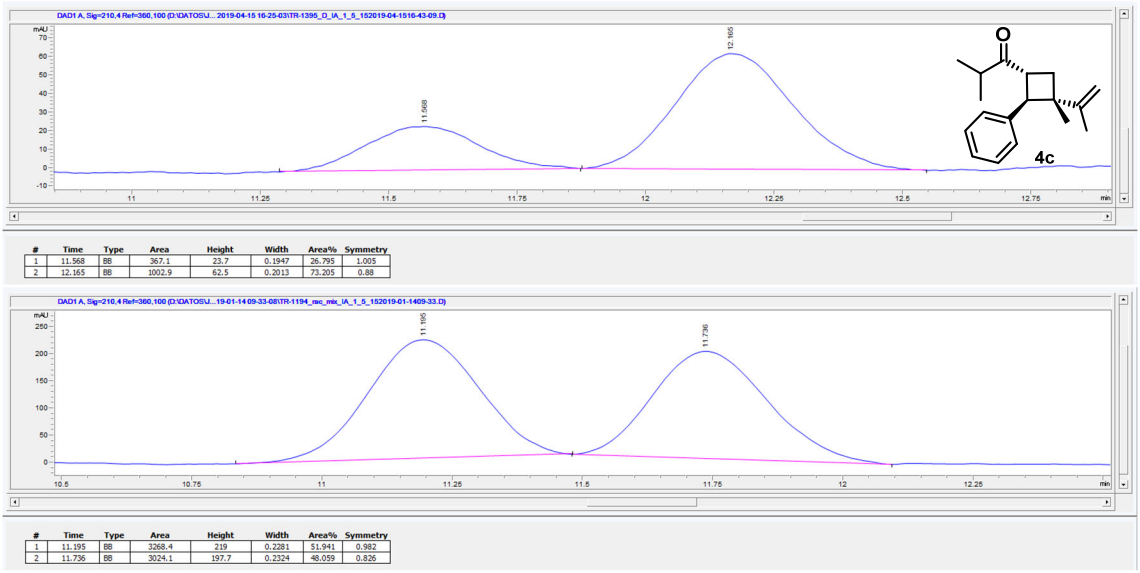


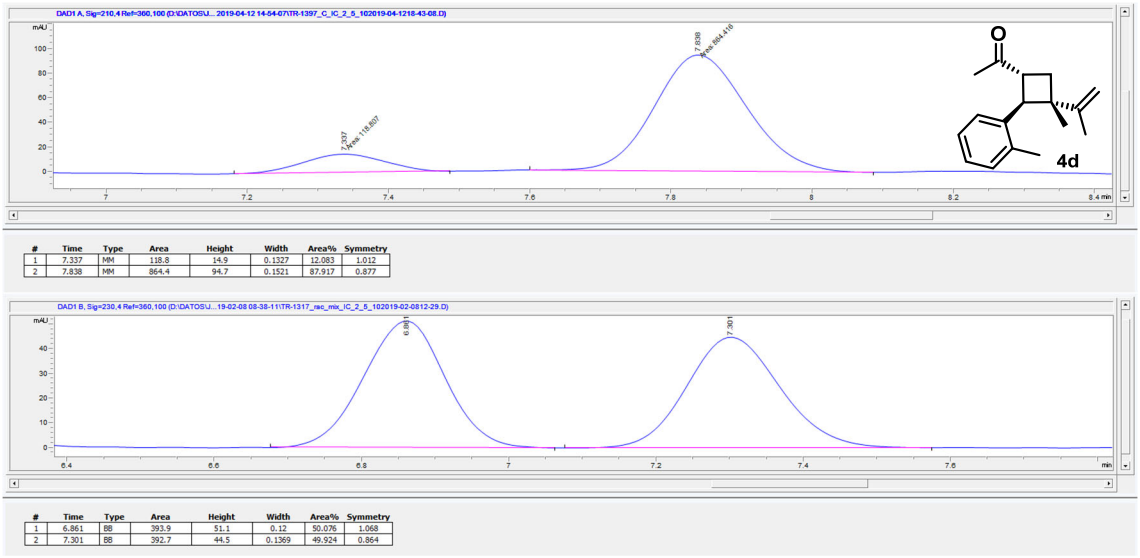
Figure S44: SFC chromatograms for compound **4b** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.568	BB	367.1	23.7	0.1947	26.795	1.005
2	12.165	BB	1002.9	62.5	0.2013	73.205	0.88

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	11.195	BB	3268.4	219	0.2281	51.941	0.982
2	11.736	BB	3024.1	197.7	0.2324	48.059	0.826

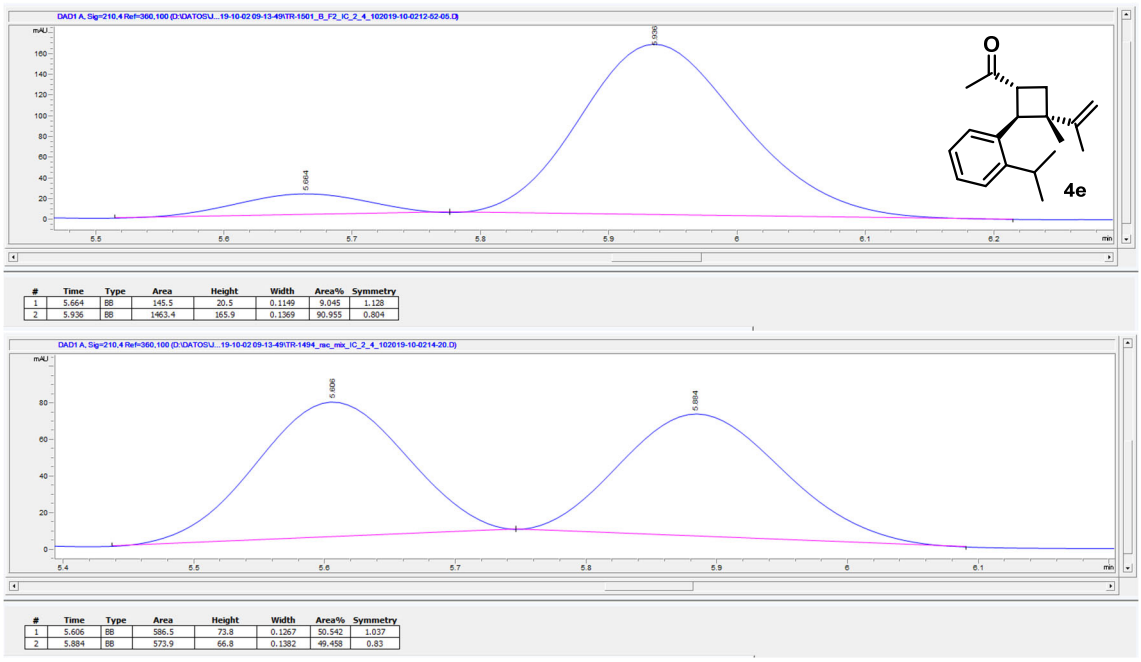
Figure S45: SFC chromatograms for compound **4c** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.337	MM	118.8	14.9	0.1327	12.083	1.012
2	7.838	MM	864.4	94.7	0.1521	87.917	0.877

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.861	BB	393.9	51.1	0.12	50.076	1.068
2	7.301	BB	392.7	44.5	0.1369	49.924	0.864

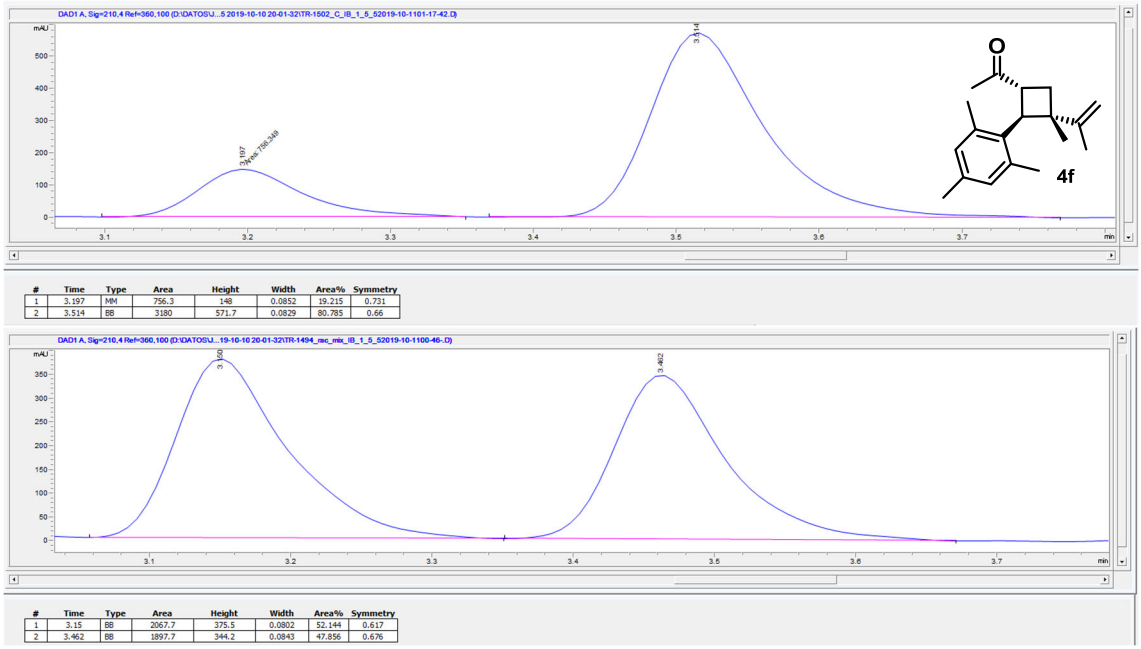
Figure S46: SFC chromatograms for compound **4d** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.664	BB	145.5	20.5	0.1149	9.045	1.128
2	5.936	BB	1463.4	165.9	0.1369	90.955	0.804

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.606	BB	586.5	73.8	0.1267	50.542	1.037
2	5.884	BB	573.9	66.8	0.1382	49.458	0.83

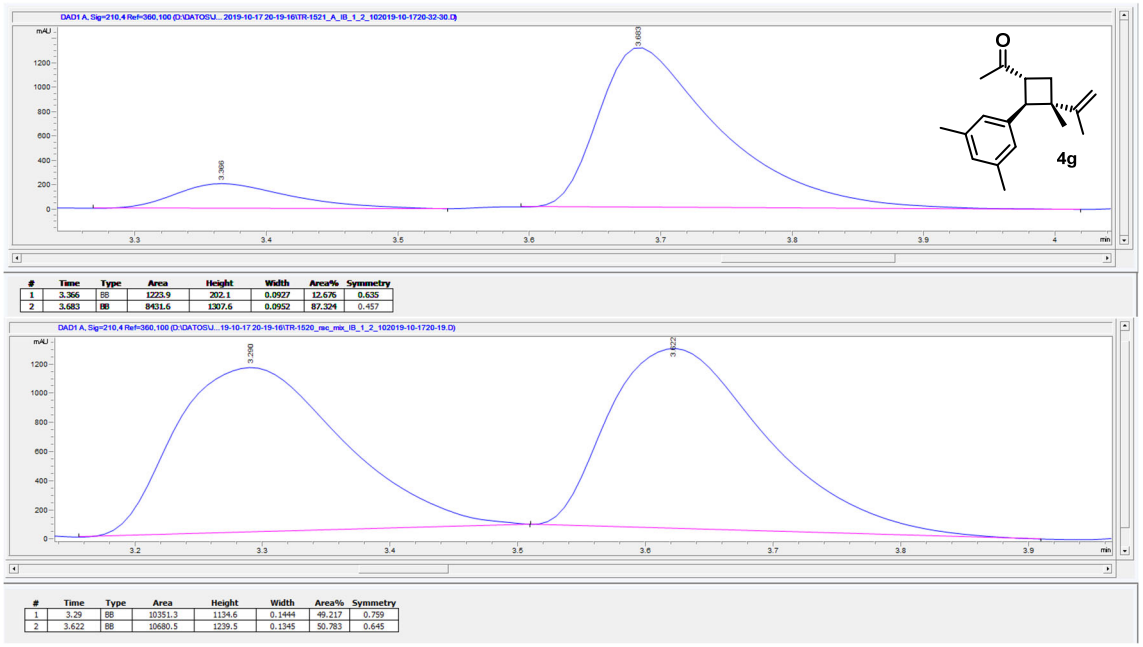
Figure S47: SFC chromatograms for compound **4e** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.197	MM	756.3	148	0.0852	19.215	0.731
2	3.514	BB	3180	571.7	0.0829	80.785	0.66

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.15	BB	2067.7	375.5	0.0802	52.144	0.617
2	3.462	BB	1897.7	344.2	0.0843	47.856	0.676

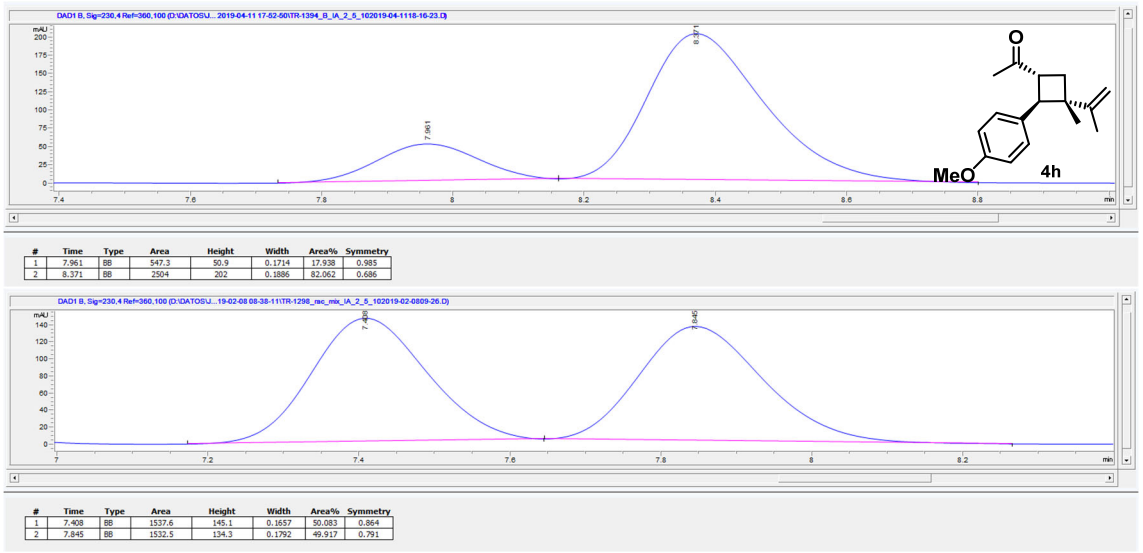
Figure S48: SFC chromatograms for compound **4f** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.366	BB	1223.9	202.1	0.0927	12.676	0.635
2	3.683	BB	8431.6	1307.6	0.0952	87.324	0.457

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.29	BB	10351.3	1134.6	0.1444	49.217	0.759
2	3.622	BB	10680.5	1239.5	0.1345	50.783	0.645

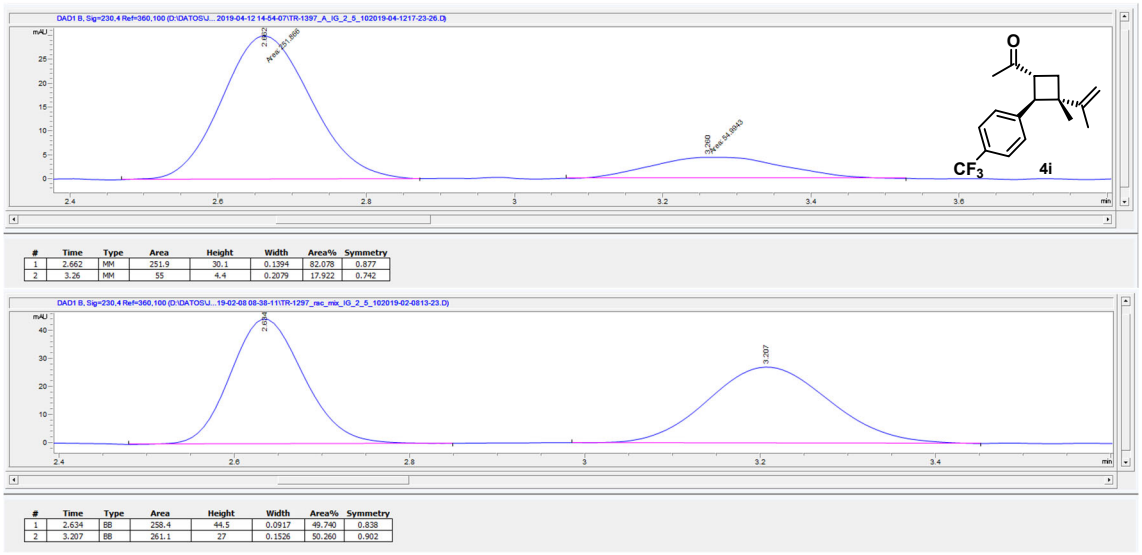
Figure S49: SFC chromatograms for compound **4g** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.961	BB	547.3	50.9	0.1714	17.938	0.985
2	8.371	BB	2504	202	0.1886	82.062	0.686

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.408	BB	1537.6	145.1	0.1657	50.083	0.864
2	7.845	BB	1532.5	134.3	0.1792	49.917	0.791

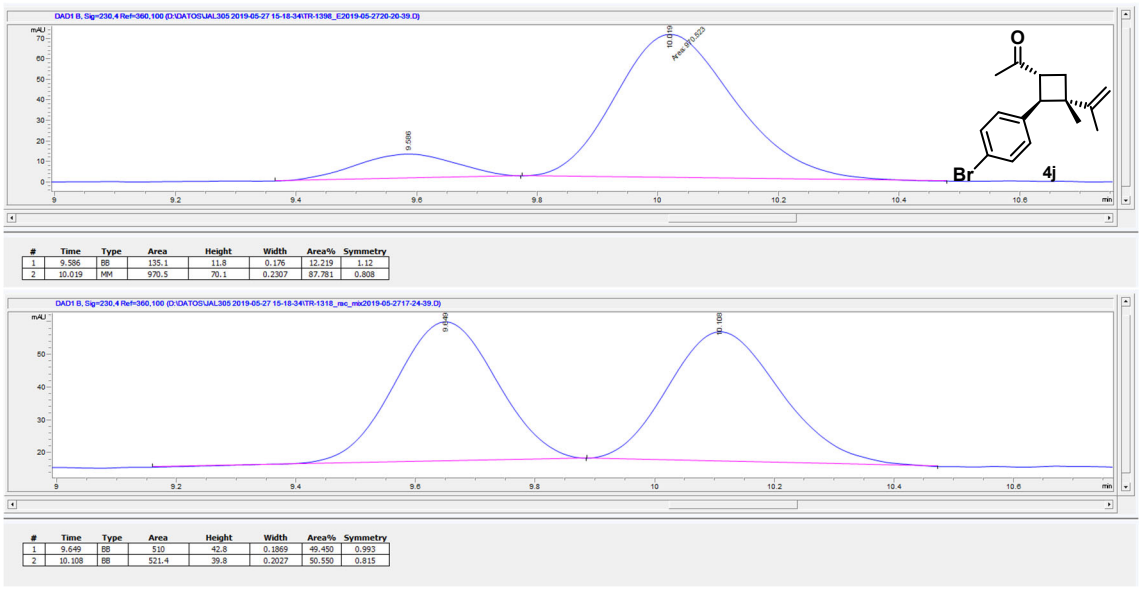
Figure S50: SFC chromatograms for compound **4h** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.662	MM	251.9	30.1	0.1394	82.078	0.877
2	3.26	MM	55	4.4	0.2079	17.922	0.742

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.634	BB	238.4	44.5	0.0917	49.740	0.838
2	3.207	BB	261.1	27	0.1526	50.260	0.902

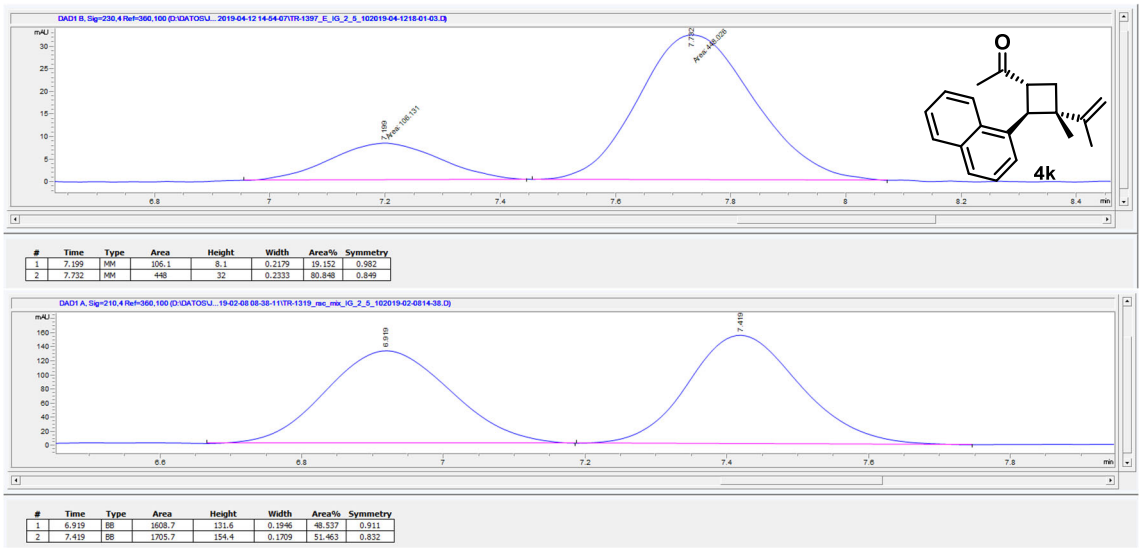
Figure S51: SFC chromatograms for compound **4i** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.586	BB	135.1	11.8	0.176	12.219	1.12
2	10.019	MM	970.5	70.1	0.2307	87.781	0.808

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	9.649	BB	510	42.8	0.1869	49.450	0.993
2	10.108	BB	521.4	39.8	0.2027	50.550	0.815

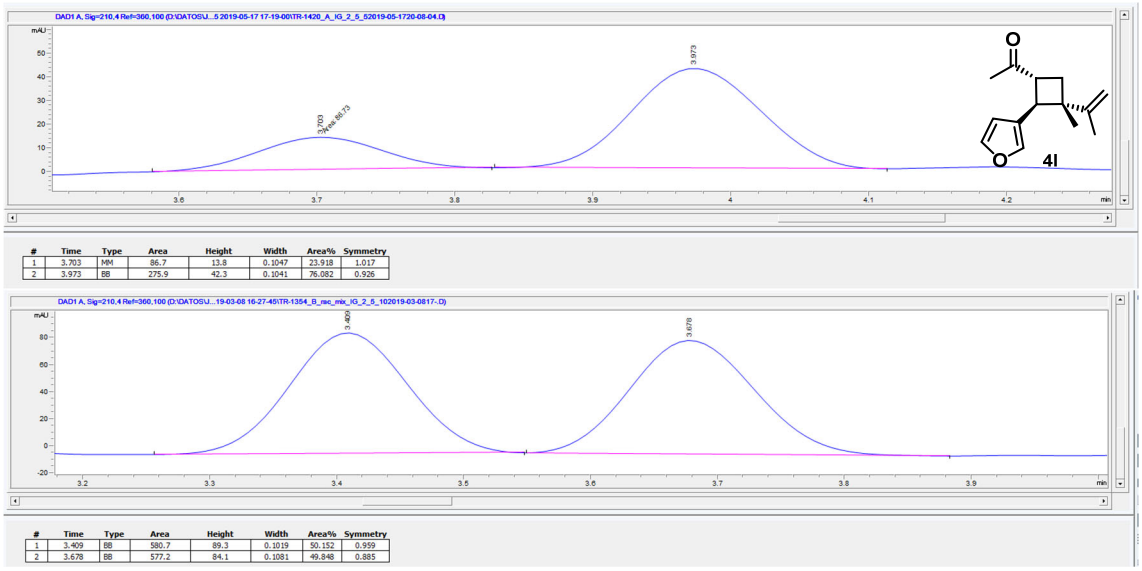
Figure S52: SFC chromatograms for compound **4j** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	7.199	MM	106.1	8.1	0.2179	19.152	0.982
2	7.732	MM	448	32	0.2333	80.848	0.849

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.919	BB	1608.7	131.6	0.1946	48.537	0.911
2	7.419	BB	1705.7	154.4	0.1709	51.463	0.832

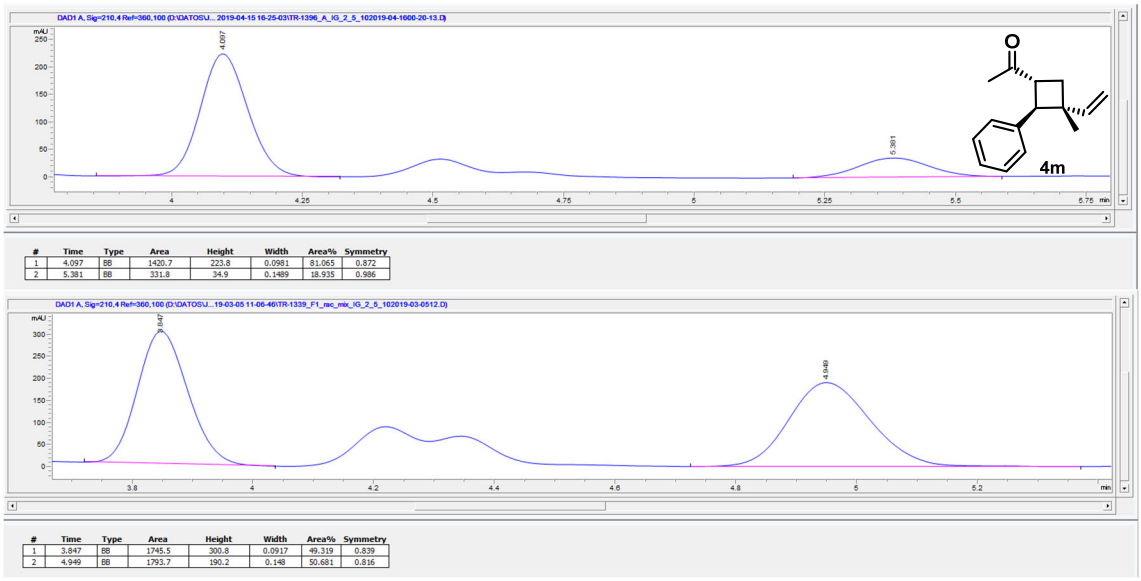
Figure S53: SFC chromatograms for compound **4k** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.703	MM	86.7	13.8	0.1047	23.918	1.017
2	3.973	BB	275.9	42.3	0.1041	76.082	0.926

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.409	BB	580.7	89.3	0.1019	50.152	0.959
2	3.678	BB	577.2	84.1	0.1081	49.848	0.885

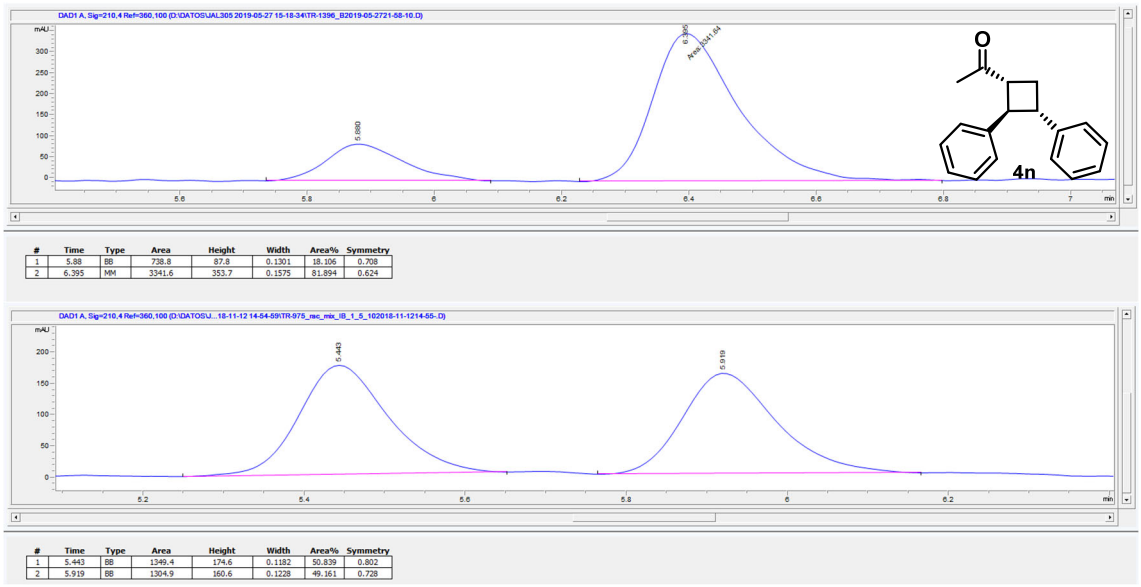
Figure S54: SFC chromatograms for compound **4l** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	4.097	BB	1420.7	223.8	0.0981	81.065	0.672
2	5.381	BB	331.8	34.9	0.1489	18.935	0.986

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	3.847	BB	1745.5	300.8	0.0917	49.319	0.839
2	4.949	BB	1793.7	190.2	0.148	50.681	0.816

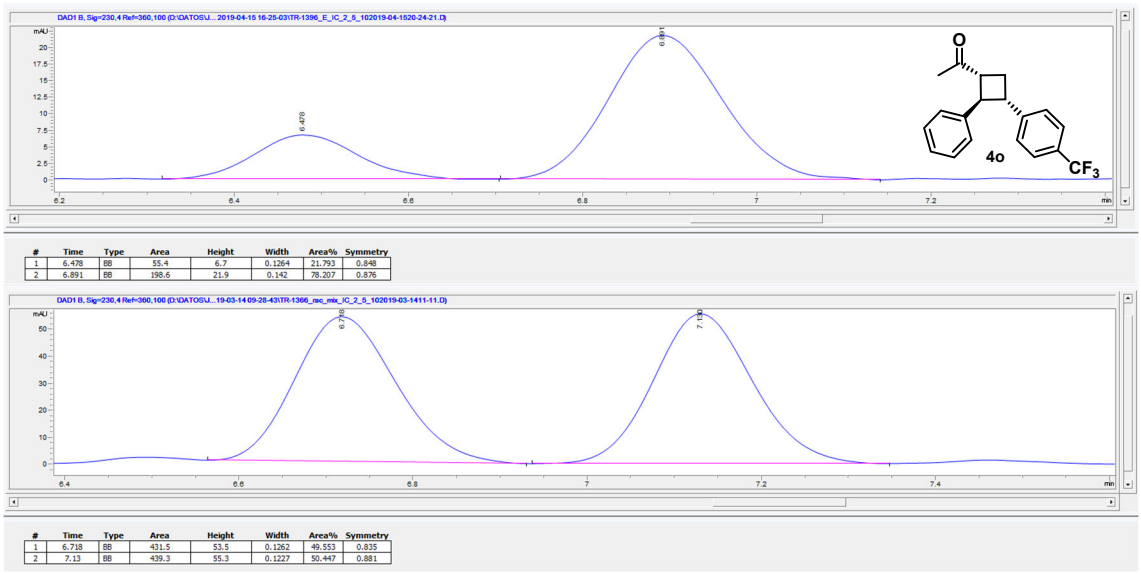
Figure S55: SFC chromatograms for compound **4m** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.88	BB	738.8	87.8	0.1301	18.106	0.708
2	6.395	MM	3341.6	353.7	0.1575	81.894	0.624

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	5.443	BB	1349.4	174.6	0.1182	50.839	0.802
2	5.919	BB	1304.9	160.6	0.1228	49.161	0.728

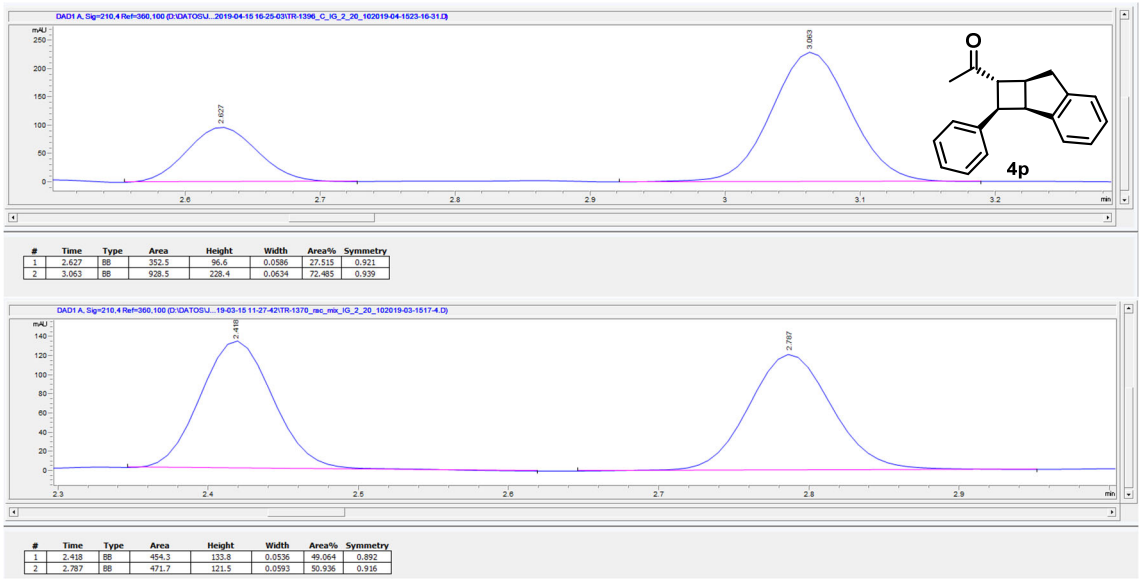
Figure S56: SFC chromatograms for compound **4n** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.478	BB	55.4	6.7	0.1264	21.793	0.848
2	6.891	BB	198.6	21.9	0.142	78.207	0.876

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	6.718	BB	431.5	53.5	0.1262	49.553	0.835
2	7.13	BB	439.3	55.3	0.1227	50.447	0.881

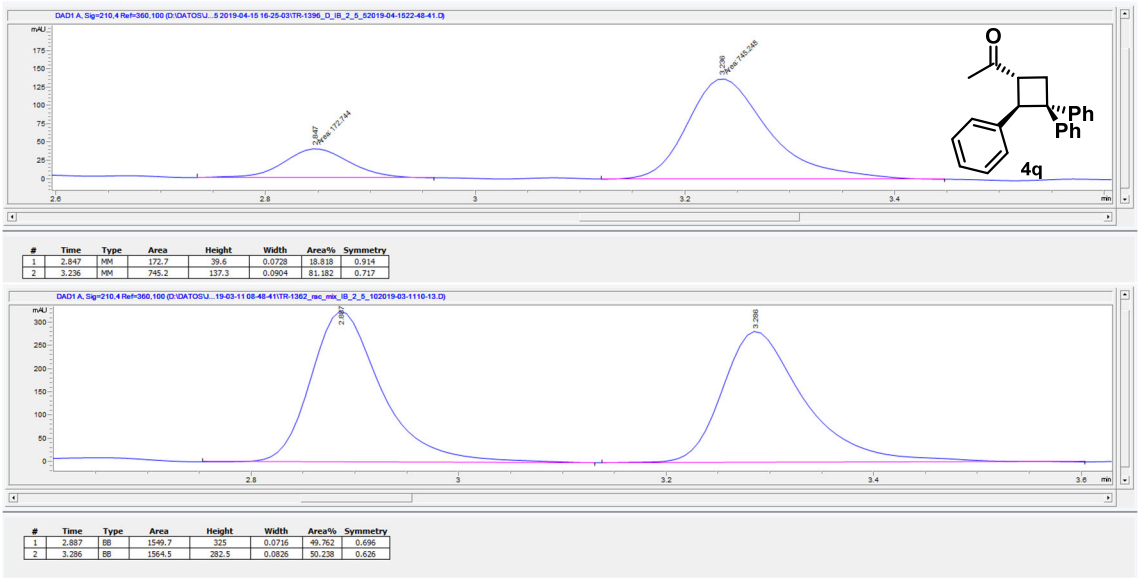
Figure S57: SFC chromatograms for compound **4o** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.627	BB	352.5	96.6	0.0586	27.515	0.921
2	3.063	BB	928.5	228.4	0.0634	72.485	0.939

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.418	BB	454.3	133.8	0.0536	49.064	0.892
2	2.787	BB	471.7	121.5	0.0593	50.936	0.916

Figure S58: SFC chromatograms for compound **4p** (enantioenriched and racemic samples).



#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.847	MM	172.7	39.6	0.0728	18.818	0.914
2	3.236	MM	745.2	137.3	0.0904	81.182	0.717

#	Time	Type	Area	Height	Width	Area%	Symmetry
1	2.887	BB	1549.7	325	0.0716	49.762	0.696
2	3.286	BB	1564.5	282.5	0.0826	50.238	0.626

Figure S59: SFC chromatograms for compound **4q** (enantioenriched and racemic samples).

9. Additional UV-Vis Absorption Spectra

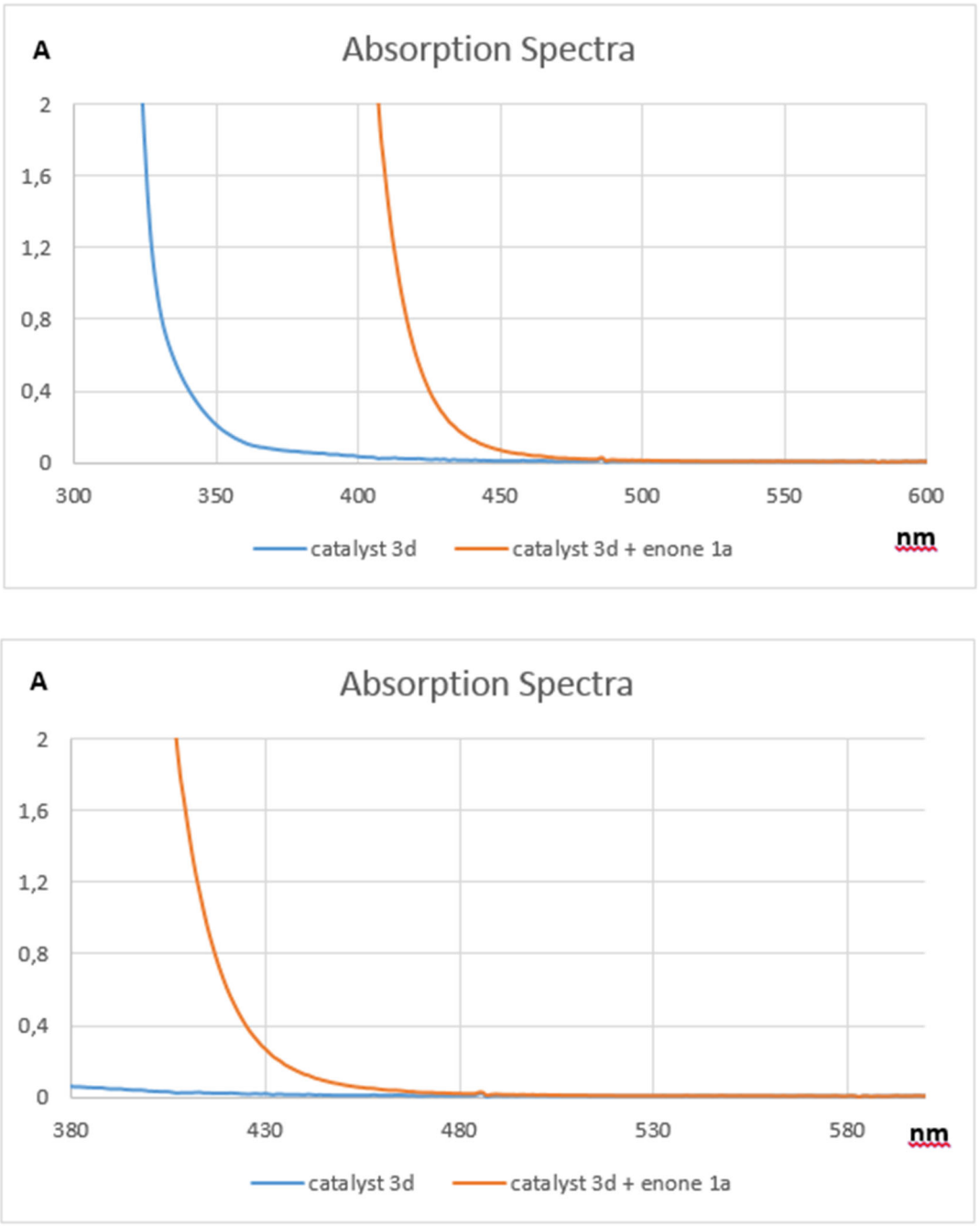


Figure S60: Additional UV-Vis Absorption Spectra (0.05 M solution: 0.1 mmol of TFA, 0.1 mmol of enone **1a**, 0.02 mmol of catalyst **3d** and 2 mL of MTBE as the solvent).

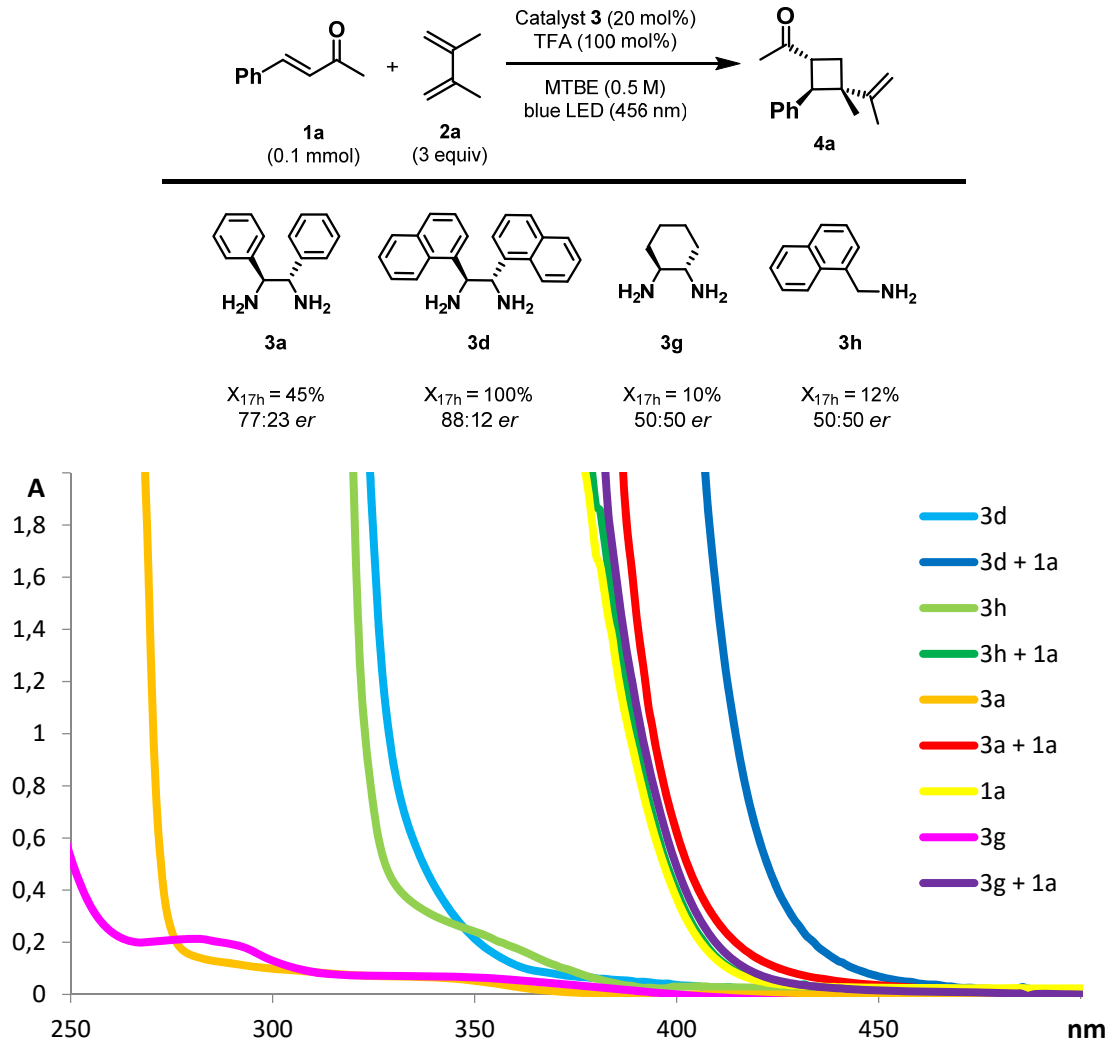


Figure S61: Additional UV-Vis Absorption Spectra (0.05 M solution: 0.1 mmol of TFA, 0.1 mmol of enone **1a** and/or 0.02 mmol of the corresponding catalyst **3** in 2 mL of MTBE as the solvent).

From an accurate observation of the UV-Vis absorption spectra (Figure S61) it can be discarded that the iminium-localized singlet excited state (LE^S) can be populated without invoking a charge transfer transition (leading to the CT^S state) and the following equilibrium between the CT^S and LE^S excited states, which allows the indirect population of the LE^S state. Indeed, a transient generated catalytic iminium ion, which lacks of the required charge-transfer interactions, and thus of a bathochromically shifted absorption band (the new charge-transfer band), cannot be responsible for the photoactivity.

Indeed, when catalyst **3h** (*light green line*), which presents an almost identical absorption profile and the same electronic nature of catalyst **3d** (*light blue line*), was employed, the reaction mixture (*green line*) did not present any absorption shift or increased absorption at longer wavelengths, leading to a low conversion (12%) upon blue LED (456 nm) irradiation (background reaction). The same behavior was observed employing catalyst **3g** (*violet line*), which led to a 10% conversion (background reaction). In both cases

(catalysts **3g** and **3h**), the absorption profile of the corresponding reaction mixture (violet and *green lines, respectively*) is identical to the one of a TFA solution of enone **1a** (*yellow line*). This is indicating that the transient generated iminium ions are not leading to a bathochromic shift or enhanced absorption at the irradiation wavelength employed in the photocatalytic reaction (456 nm).

This is due to the fact that the amount of iminium ion that is present in the reaction mixture is really small (a well-known fact in organocatalysis and iminium ion catalysis) and this effect is even more accentuated when a primary amine is employed, in comparison with secondary amines such as imidazolidinone or pyrrolidine-based catalysts, due to a reduced nucleophilicity and less effective stabilization of the iminium ion by hyperconjugation.[7] Nevertheless, despite its low abundance in the reaction mixture, the iminium ion is efficiently formed for both catalysts **3g** and **3h**, as evidenced by the fact that the reaction can work with the use of a 0.2 mol% of an external ruthenium photosensitizer (leading to 68% and 58% conversion in the case of catalyst **3g** and **3h**, respectively). Thus, this indicates that, despite its formation, the iminium ion itself is not responsible for the absorption at the employed irradiation wavelength and that the reaction requires the presence of a bathochromically shifted charge-transfer band to efficiently excite the catalytic species to the iminium-localized singlet excited state (LE^S) by means of the well-known equilibrium between localized and charge-transfer excited species present in the excited state.[8] Indeed, the charge-transfer interactions and the corresponding charge-transfer transition is only observed for catalysts bearing an electron-rich moiety (catalyst **3d** or, to a slightly extent, catalyst **3a**) which has to be in close proximity of the electron-poor one due to steric constrains present upon iminium ion formation. Catalyst **3h** is not giving any CT complex in the excited state because the steric constrains are completely different from the case of catalyst **3d**, allowing the disposition of the two moieties (electron-donor and electron-acceptor) far away from each other, leading to an absent charge transfer interaction in the excited state, as expected. In addition, catalyst **3a** which presents an absorption profile hypsochromically shifted in comparison with catalyst **3h**, is giving, a slight corresponding bathochromic absorption shift (in the reaction mixture) which can be due just to the slight formation of a CT complex in the excited state, evidencing once again that the absorption profile of the sole catalyst is not having an important effect on the resulting absorption of the corresponding reaction mixture (only the presence of a CT complex in the excited state is enhancing the absorption at longer wavelengths).

10. Evidences on the Nature of the Reactive Species in the [2+2] Photocycloaddition (Discrimination between B-1 and B-2)

To determine which of the two possible singlet excited species (**B-1** or **B-2**, Figure 3 of the main manuscript) is responsible of the observed reactivity in the [2+2] photocycloaddition we analyzed the possible different reaction pathways that could originate from the two investigated species.

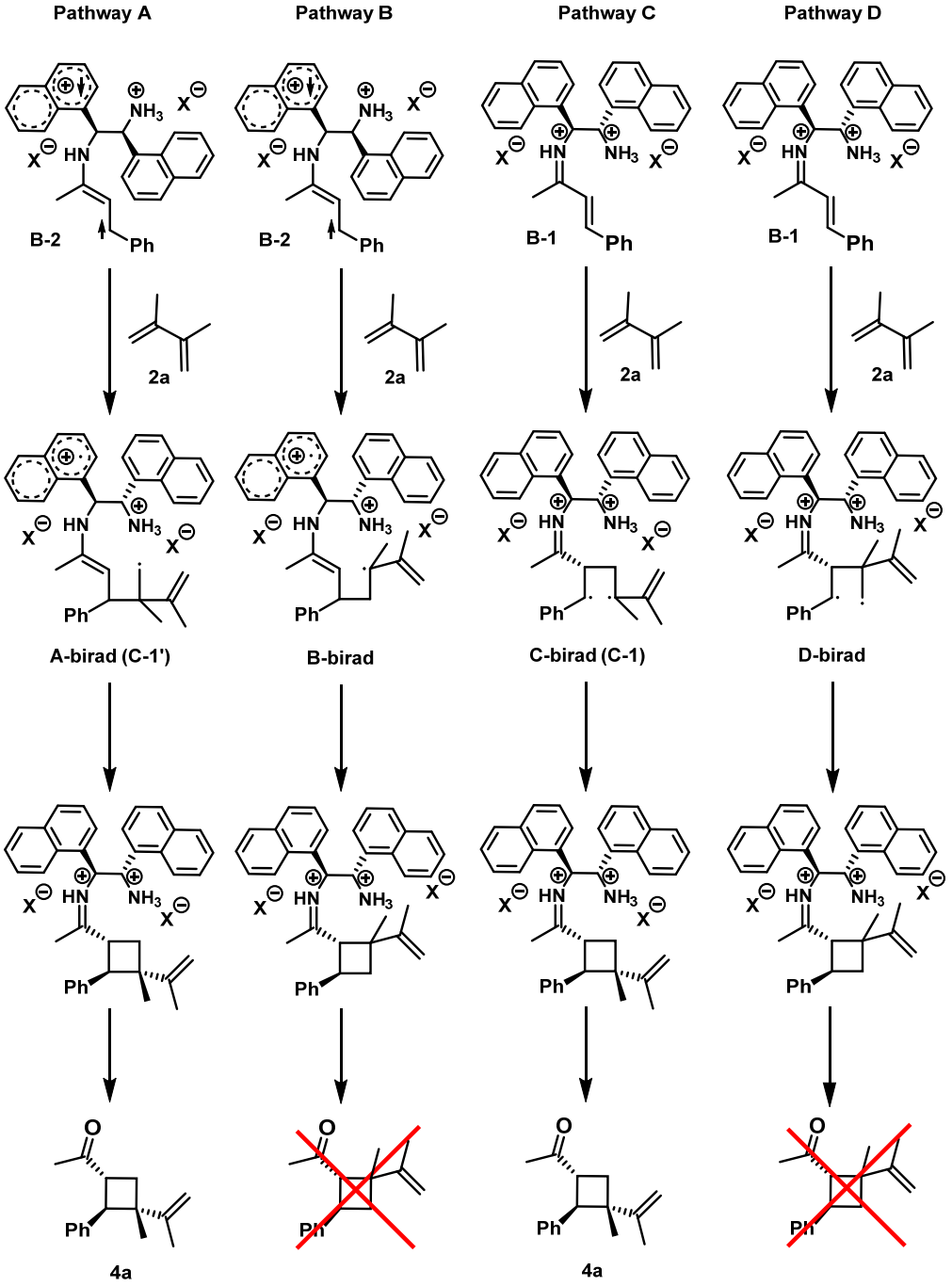


Figure S62: Different hypothetical pathways for the [2+2] photocycloaddition.

Although all the mechanisms seem to be possible pathways for the reaction, the regioselectivity experimentally observed in the product (only the two epimers at the cyclobutane quaternary carbon are obtained) is clearly discarding pathway **B** and **D**. Furthermore, pathway **A** would lead to a biradical intermediate **A-birad (C-1')** that it is significantly less stable (by 20.6 kcal/mol) than biradical **C-birad** (biradical **C-1**, Figure 3 of the main manuscript), as observed from DFT Calculations (Figure 5-bottom of the main manuscript and *vide infra* for DFT data). This is quite obvious since the formation of a primary radical is strongly disfavored and unlikely. All these evidences are indicating as pathway **C** as the only one occurring, demonstrating that **B-1** is the reactive species and **B-2** an unproductive one in the [2+2] photocycloaddition.

11. Evidences of Singlet Excited State Reactivity of Iminium Ion B-1

As described in the main text of the manuscript, the presence of oxygen did not inhibit the reaction, observing full conversion after 17 hours (Table 1). This indicates that the reactive species is in its singlet excited state.

Furthermore, the stereochemical outcome of the reaction was significantly different when $Ru(bpy)_3Cl_2 \cdot 6H_2O$ was employed as a triplet photosensitizer, being, as expected, in contrast with the singlet reactivity that we propose since an excited triplet iminium ion is supposed to be the reactive species in this case. Indeed, the diastereoisomeric ratio observed in product **4k** (*dr* = 5:1) was significantly different from the one observed in the absence of the ruthenium photosensitizer (*dr* = 2:1) because of the different nature of the excited intermediates (triplet vs singlet excited state reactivity, Figure 4 of the main manuscript and Figure S63). Product **4k** was properly chosen for this comparison because of the low *dr* obtained without an external photocatalyst (Table 2). The different diastereoisomeric ratios observed in the two cases are in accordance with the different reaction mechanism (triplet vs singlet, Figure S63). The triplet pathway is a stepwise mechanism whereas the singlet pathway can be a stepwise or a concerted mechanism. The important difference is that the *triplet biradical* is supposed to exist for a longer time since it is necessary for it to undergo an intersystem crossing to a singlet state before being able of forming the second C-C bond of the cyclobutane ring. Thus, the different lifetime of this intermediate is responsible of the higher diastereoisomeric ratio observed, since it is easily understandable that a longer lifetime can permit a higher degree of organization of the biradical to place the bulkier substituent (*i*-propenyl) trans to the

aromatic substituent (naphthyl) of the cyclobutane ring. In addition, it is worthwhile to remember that the enone substrate **1a** presents a higher energy gap that does not allow the reaction to proceed in the absence of a diamine catalyst, which enables the formation of the iminium ion (conversion <10%). Furthermore, the enantiomeric excesses obtained from the singlet excited state reactivity and from the triplet photosensitized reaction were comparable, indicating once again the intermediacy of an iminium ion catalyzed reaction in both the pathways

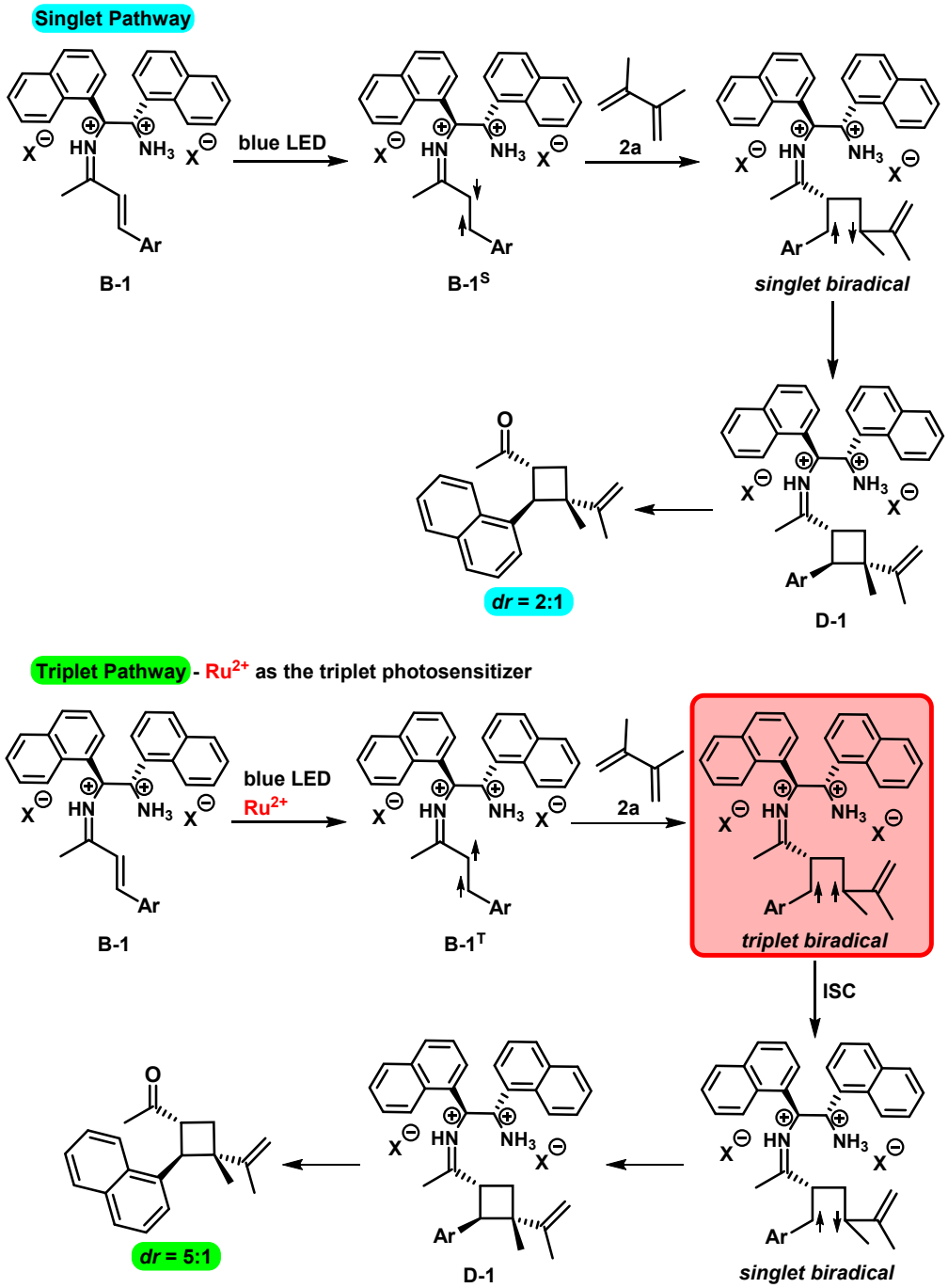
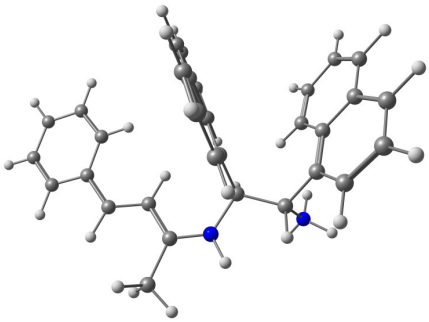


Figure S63: Different diastereoselectivity of singlet and triplet mechanisms.

12. Computational Details

Quantum chemistry calculations were carried out using the density functional theory (DFT). In particular, geometry optimizations were performed using the M06-2X functional[9] in combination with the 6-311G** basis set[10] including methyl *tert*-butyl ether ($\varepsilon = 2.6$) solvent effects with the solvation model density (SMD).[11] All optimizations were performed without any geometrical constraint and harmonic vibrational frequencies have been also evaluated at the same level of theory to characterize minima and transition states in the potential energy surface. Transition states have been connected to products by optimization of geometries slightly modified from the transition states. All the calculations were performed using the Gaussian09 program.[12] The energies in the energetic profiles in the main text are given in kcal/mol. The energies of the structures are given in hartree/particle. Electronic excitations ($S_0 \rightarrow T_{1\text{-}6}$ and $S_0 \rightarrow S_{1\text{-}6}$) were evaluated using CAMB3LYP functional in combination with the 6-31G* basis set performing single point calculations on optimized geometries at M06-2X/6-311G** level.



(alternative structure found, but less stable, for species A1)

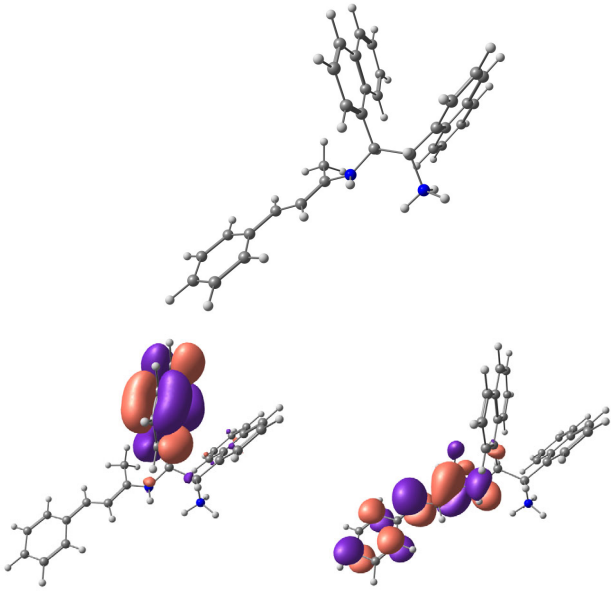
Charge = 2 Multiplicity = 1

Sum of electronic and thermal Free Energies= -1345.839352

6	-2.028369000	2.067562000	-0.706851000
1	-2.083985000	3.036017000	-0.209773000
6	-0.553964000	1.552800000	-0.591735000
1	-0.241532000	1.137872000	-1.552488000
6	-0.385931000	0.521310000	0.512728000
6	-0.701193000	0.903735000	1.793831000
6	0.066189000	-0.808574000	0.244584000
6	-0.613896000	0.002366000	2.872102000
6	0.160595000	-1.710588000	1.343780000

6	-0.196814000	-1.280739000	2.645621000
1	-1.041765000	1.917854000	1.984863000
1	-0.880589000	0.329503000	3.868617000
6	-3.138271000	1.233399000	-0.116548000
6	-3.417415000	-0.100595000	-0.546360000
6	-3.890935000	1.814063000	0.877155000
6	-4.479720000	-0.800391000	0.093842000
6	-4.939618000	1.113283000	1.508724000
6	-5.222715000	-0.166688000	1.123584000
1	-3.672060000	2.826672000	1.202198000
1	-5.508402000	1.595309000	2.292953000
6	0.461826000	-1.286662000	-1.037410000
6	0.908310000	-2.569897000	-1.213009000
6	0.622400000	-3.036506000	1.127379000
6	0.987765000	-3.462156000	-0.119581000
1	1.208068000	-2.903104000	-2.199262000
1	0.680236000	-3.706023000	1.978277000
1	1.338217000	-4.474802000	-0.274236000
6	-2.697618000	-0.773317000	-1.566572000
6	-4.777010000	-2.128714000	-0.301193000
6	-3.006172000	-2.059334000	-1.927359000
6	-4.060103000	-2.747265000	-1.289514000
1	-5.585289000	-2.648736000	0.200186000
1	-2.429560000	-2.555160000	-2.698632000
1	-4.293520000	-3.763106000	-1.581727000
7	0.296334000	2.748175000	-0.352660000
7	-2.365351000	2.379291000	-2.163263000
1	-2.518087000	1.515444000	-2.696097000
1	-1.646989000	2.930418000	-2.642705000
6	1.609403000	2.785103000	-0.212224000
6	2.197910000	4.116344000	0.141970000
1	2.572185000	4.085066000	1.167504000
1	3.031900000	4.355782000	-0.517196000
1	1.458099000	4.911952000	0.068999000

6	2.395890000	1.613549000	-0.352086000
1	1.904952000	0.688143000	-0.609416000
6	3.738577000	1.611764000	-0.114718000
1	4.240557000	2.552948000	0.096177000
6	4.584545000	0.444416000	-0.108362000
6	4.060370000	-0.862582000	-0.110185000
6	5.977495000	0.627682000	-0.080824000
6	4.914180000	-1.949023000	-0.110645000
6	6.828560000	-0.465675000	-0.093494000
6	6.296826000	-1.752135000	-0.110633000
1	2.989925000	-1.029993000	-0.079897000
1	6.383101000	1.632951000	-0.058943000
1	4.508577000	-2.953060000	-0.100421000
1	7.900816000	-0.319197000	-0.082298000
1	6.960435000	-2.608394000	-0.111507000
1	-6.024387000	-0.719497000	1.600130000
1	-1.852860000	-0.302201000	-2.057802000
1	-0.125359000	-1.989483000	3.462598000
1	0.431450000	-0.643328000	-1.908761000
1	-3.245175000	2.904303000	-2.206521000
1	-0.182434000	3.624380000	-0.179349000



HOMO LUMO

Charge = 2 Multiplicity = 1

Sum of electronic and thermal Free Energies= -1345.840184

6	0.997140000	-1.220716000	1.421683000
1	0.678268000	-0.852205000	2.398690000
6	0.211207000	-0.423701000	0.357621000
1	0.464368000	-0.779658000	-0.637334000
6	0.572283000	1.049349000	0.510626000
6	0.028116000	1.744414000	1.564002000
6	1.515334000	1.678054000	-0.360629000
6	0.382341000	3.084054000	1.822594000
6	1.880660000	3.028168000	-0.080296000
6	1.296841000	3.706399000	1.019072000
1	-0.688766000	1.270165000	2.227156000
1	-0.067175000	3.605028000	2.658038000
6	2.492322000	-1.066051000	1.309820000
6	3.234181000	-1.594117000	0.203850000
6	3.124367000	-0.343938000	2.293583000
6	4.636522000	-1.346275000	0.171944000
6	4.510614000	-0.095926000	2.245070000
6	5.246882000	-0.590332000	1.205422000
1	2.545337000	0.058040000	3.118511000

1	4.979646000	0.481534000	3.030745000
6	2.115722000	1.044117000	-1.482580000
6	3.032934000	1.703402000	-2.258054000
6	2.831020000	3.681989000	-0.905665000
6	3.401862000	3.035431000	-1.966669000
1	3.480010000	1.197256000	-3.105089000
1	3.095528000	4.707757000	-0.675138000
1	4.129804000	3.540547000	-2.588788000
6	2.674392000	-2.335462000	-0.876502000
6	5.414459000	-1.841295000	-0.905405000
6	3.454069000	-2.801741000	-1.904493000
6	4.842845000	-2.556276000	-1.922125000
1	6.479024000	-1.637314000	-0.907308000
1	2.997112000	-3.356535000	-2.714821000
1	5.446081000	-2.928842000	-2.739860000
7	-1.231705000	-0.651601000	0.546381000
7	0.633387000	-2.705122000	1.435370000
1	1.180363000	-3.229587000	0.744706000
1	-0.360792000	-2.879358000	1.258720000
6	-2.166192000	-0.411619000	-0.367344000
6	-1.713522000	-0.081742000	-1.748958000
1	-2.539786000	0.119656000	-2.420223000
1	-1.063863000	0.798540000	-1.716296000
1	-1.134885000	-0.912816000	-2.161554000
6	-3.519719000	-0.478327000	0.050301000
1	-3.691717000	-0.725865000	1.092293000
6	-4.580342000	-0.223624000	-0.767407000
1	-4.392946000	0.043492000	-1.802390000
6	-5.973324000	-0.259113000	-0.404441000
6	-6.426659000	-0.625557000	0.877308000
6	-6.912893000	0.092382000	-1.389327000
6	-7.779109000	-0.634689000	1.156471000
6	-8.268211000	0.085653000	-1.103527000
6	-8.700055000	-0.277454000	0.168436000

1	-5.725379000	-0.907824000	1.652642000
1	-6.566803000	0.372973000	-2.377845000
1	-8.127194000	-0.919089000	2.141073000
1	-8.985862000	0.360609000	-1.865474000
1	-9.759205000	-0.285110000	0.395649000
1	6.314373000	-0.409933000	1.151974000
1	1.607754000	-2.521800000	-0.951076000
1	1.589065000	4.732785000	1.210227000
1	1.866059000	0.025718000	-1.750005000
1	0.867421000	-3.105019000	2.349564000
1	-1.564146000	-0.718828000	1.504662000

TDDFT (CAMB3LYP/631G*) transitions analysis (Excitation energies and oscillator strengths):

Excited State 1: Triplet **2.0127 eV** 616.00 nm f=0.0000 <S**2>=2.000

107 ->118 -0.11361

109 ->118 0.11264

112 ->125 0.10743

114 ->118 0.65824 (HOMO-3-LUMO transition)

117 ->118 0.11773

114 <-118 0.13295

Excited State 2: Triplet 2.5518 eV 485.86 nm f=0.0000 <S**2>=2.000

111 ->127 0.15828

115 ->123 -0.19866

117 ->120 0.61705

117 ->124 -0.11304

117 <-120 0.13817

Excited State 3: Triplet 2.5961 eV 477.58 nm f=0.0000 <S**2>=2.000

110 ->126 0.12258

113 ->122 -0.20018

116 ->119 0.62953

117 ->119 0.12063

116 <-119 0.13928

Excited State 4: Triplet 3.1305 eV 396.06 nm f=0.0000 <S**2>=2.000

112 ->118 0.66367

112 ->121 0.19953

Excited State 5: Singlet 3.2424 eV **382.39 nm f=0.2685** <S**2>=0.000

114 ->118 0.21247

117 ->118 0.66142 (HOMO-LUMO transition)

Excited State 6: Triplet 3.2519 eV 381.26 nm f=0.0000 <S**2>=2.000

114 ->118 -0.11248

117 ->118 0.66192

Excited State 7: Singlet 3.5508 eV **349.17 nm f=1.1498** <S**2>=0.000

113 ->118 0.10500

114 ->118 0.64968 (HOMO-3-LUMO transition)

117 ->118 -0.21145

Excited State 8: Triplet 3.7740 eV 328.52 nm f=0.0000 <S**2>=2.000

95 ->118 -0.11562

107 ->118 -0.26873

109 ->118 0.40162

112 ->125 -0.26735

114 ->121 -0.25954

114 ->130 -0.10181

117 ->118 -0.12607

Excited State 9: Singlet 3.8588 eV 321.30 nm f=0.0437 <S**2>=0.000

112 ->118 0.69014

Excited State 10: Singlet 3.9891 eV 310.81 nm f=0.0000 <S**2>=0.000

115 ->118 -0.13385

116 ->118 0.68675

Excited State 11: Singlet 4.1258 eV 300.51 nm f=0.0026 <S**2>=0.000

115 ->118 0.68289

116 ->118 0.13334

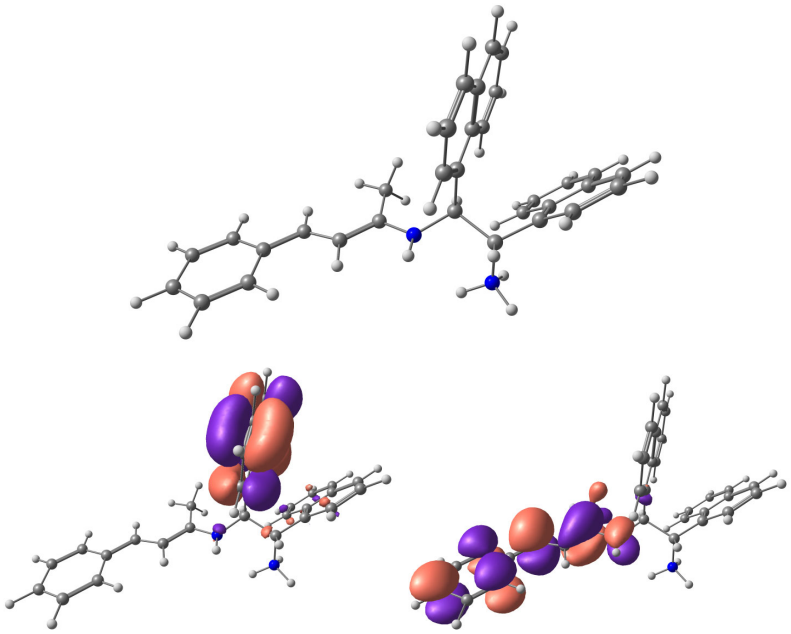
Excited State 12: Singlet 4.5101 eV 274.90 nm f=0.1138 <S**2>=0.000

115 ->120 -0.13631

116 ->119 0.29611

117 ->119 0.30574

117 ->120 0.49493



SOMO-1 SOMO-2

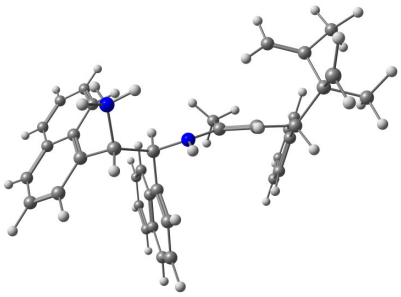
Charge = 2 Multiplicity = 3

Sum of electronic and thermal Free Energies= -1345.762736

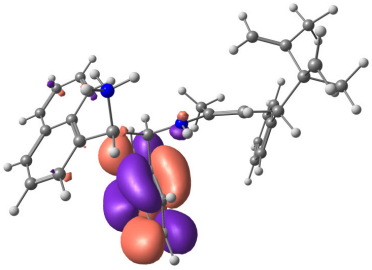
6	-1.041049000	-1.218847000	-1.484451000
1	-0.713636000	-0.835063000	-2.452802000
6	-0.229728000	-0.480358000	-0.399073000
1	-0.509475000	-0.847766000	0.583539000
6	-0.535737000	1.009449000	-0.514546000
6	0.002267000	1.703339000	-1.572264000
6	-1.417992000	1.661718000	0.401724000
6	-0.293936000	3.064228000	-1.787207000
6	-1.722743000	3.035657000	0.168804000
6	-1.143728000	3.712083000	-0.933890000
1	0.668179000	1.210628000	-2.274655000
1	0.148498000	3.582779000	-2.627985000
6	-2.529622000	-1.018713000	-1.361826000
6	-3.282306000	-1.530673000	-0.255629000
6	-3.142301000	-0.259944000	-2.329870000
6	-4.673848000	-1.229435000	-0.207643000
6	-4.517551000	0.041026000	-2.266139000
6	-5.263454000	-0.437124000	-1.225841000

1	-2.553758000	0.129669000	-3.153821000
1	-4.970085000	0.647109000	-3.039817000
6	-2.017525000	1.027190000	1.523670000
6	-2.872706000	1.710507000	2.347652000
6	-2.610362000	3.713907000	1.043140000
6	-3.178105000	3.068304000	2.106434000
1	-3.320027000	1.203570000	3.194071000
1	-2.830873000	4.757194000	0.847570000
1	-3.857025000	3.592912000	2.766795000
6	-2.743004000	-2.311528000	0.806852000
6	-5.461218000	-1.709777000	0.869481000
6	-3.531609000	-2.764117000	1.834008000
6	-4.909393000	-2.463623000	1.868995000
1	-6.516879000	-1.463742000	0.884653000
1	-3.090588000	-3.351244000	2.630241000
1	-5.519782000	-2.825281000	2.686356000
7	1.198222000	-0.764722000	-0.569449000
7	-0.712689000	-2.708334000	-1.532958000
1	-1.268880000	-3.239145000	-0.855028000
1	0.279727000	-2.894194000	-1.354271000
6	2.116892000	-0.577882000	0.417531000
6	1.626946000	-0.393977000	1.814577000
1	2.448975000	-0.245335000	2.507151000
1	0.972436000	0.481901000	1.873056000
1	1.057322000	-1.266562000	2.149238000
6	3.472464000	-0.563109000	0.041404000
1	3.666208000	-0.667188000	-1.022810000
6	4.580238000	-0.431887000	0.905899000
1	4.419175000	-0.393941000	1.974845000
6	5.903578000	-0.337829000	0.457147000
6	6.290862000	-0.341611000	-0.935971000
6	6.957851000	-0.220603000	1.438332000
6	7.605685000	-0.253683000	-1.294690000
6	8.264190000	-0.131663000	1.062024000

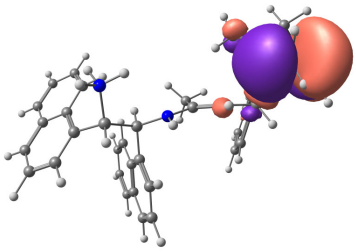
6	8.612825000	-0.149558000	-0.311098000
1	5.537746000	-0.409155000	-1.708415000
1	6.683523000	-0.207424000	2.486207000
1	7.883664000	-0.258955000	-2.340898000
1	9.042890000	-0.045259000	1.808893000
1	9.651474000	-0.081639000	-0.606689000
1	-6.322648000	-0.216130000	-1.160179000
1	-1.683646000	-2.539846000	0.867315000
1	-1.388189000	4.756807000	-1.088944000
1	-1.817067000	-0.011318000	1.751989000
1	-0.947340000	-3.084253000	-2.456275000
1	1.556079000	-0.696502000	-1.517687000



Biradical species C-1’



SOMO-1



SOMO-2

Charge = 2 Multiplicity = 3

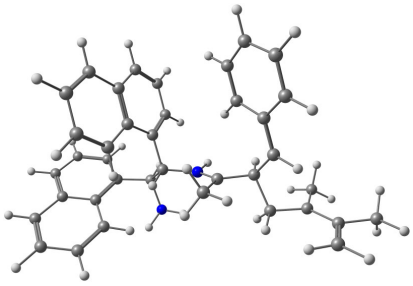
Sum of electronic and thermal Free Energies= -1580.193197

6	-1.948485000	-1.580645000	-1.497829000
1	-1.876405000	-1.398701000	-2.572090000
6	-0.947940000	-0.644613000	-0.788154000
1	-0.993358000	-0.803911000	0.282963000

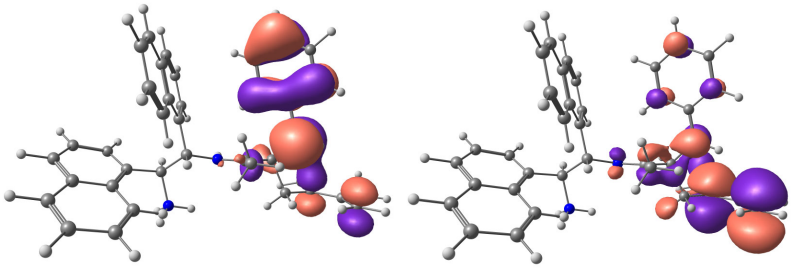
6	-1.308255000	0.799405000	-1.119384000
6	-1.047169000	1.262494000	-2.388013000
6	-1.943537000	1.642530000	-0.156246000
6	-1.387220000	2.574664000	-2.773844000
6	-2.289942000	2.966692000	-0.559353000
6	-1.997020000	3.405316000	-1.874422000
1	-0.577185000	0.621314000	-3.128774000
1	-1.168699000	2.912578000	-3.778412000
6	-3.368098000	-1.351402000	-1.044527000
6	-3.792984000	-1.665122000	0.287706000
6	-4.240281000	-0.780970000	-1.940037000
6	-5.144085000	-1.375614000	0.635238000
6	-5.571351000	-0.488053000	-1.579937000
6	-6.009664000	-0.784025000	-0.319968000
1	-3.899754000	-0.535929000	-2.940654000
1	-6.234438000	-0.034568000	-2.304731000
6	-2.260977000	1.245953000	1.171797000
6	-2.885585000	2.107340000	2.034650000
6	-2.933302000	3.833404000	0.361281000
6	-3.228872000	3.416182000	1.629144000
1	-3.120661000	1.779838000	3.040045000
1	-3.189083000	4.834879000	0.035005000
1	-3.722694000	4.082947000	2.324623000
6	-2.965555000	-2.237517000	1.297632000
6	-5.613768000	-1.667225000	1.941095000
6	-3.450549000	-2.509266000	2.551821000
6	-4.792082000	-2.225257000	2.881845000
1	-6.645688000	-1.435161000	2.179023000
1	-2.793935000	-2.939059000	3.298293000
1	-5.161674000	-2.445025000	3.875055000
7	0.430276000	-0.942476000	-1.208748000
7	-1.594163000	-3.059215000	-1.338856000
1	-1.993950000	-3.446984000	-0.477131000
1	-0.584536000	-3.235778000	-1.331030000

6	1.520350000	-0.602289000	-0.506434000
6	1.343814000	-0.212927000	0.923562000
1	2.300177000	-0.126173000	1.427199000
1	0.814259000	0.744494000	0.991078000
1	0.751112000	-0.975637000	1.436259000
6	2.751554000	-0.679633000	-1.192877000
1	2.719905000	-1.193975000	-2.151460000
6	4.072478000	-0.080342000	-0.856429000
1	4.330007000	0.410798000	-1.811437000
6	3.999205000	1.042350000	0.165433000
6	3.271583000	2.180083000	-0.198866000
6	4.573211000	0.994297000	1.435324000
6	3.092451000	3.231151000	0.692026000
6	4.401220000	2.049632000	2.325901000
6	3.654724000	3.165374000	1.962463000
1	2.843009000	2.246347000	-1.195123000
1	5.139325000	0.129372000	1.753392000
1	2.524414000	4.103034000	0.390920000
1	4.853471000	1.995869000	3.308666000
1	3.523682000	3.982886000	2.660412000
1	-7.031098000	-0.568705000	-0.027661000
1	-1.912904000	-2.442115000	1.130807000
1	-2.270097000	4.415856000	-2.156822000
1	-2.028754000	0.252397000	1.532584000
1	-2.001580000	-3.593240000	-2.112164000
1	0.573754000	-1.096404000	-2.203592000
6	4.003752000	-2.600905000	0.913868000
6	5.134024000	-1.998518000	0.552113000
6	5.233749000	-1.148099000	-0.726441000
6	5.173223000	-2.071170000	-1.913740000
1	5.175424000	-1.644063000	-2.912240000
1	3.966832000	-3.240894000	1.787562000
1	3.086682000	-2.516335000	0.340775000
1	5.474350000	-3.104125000	-1.802321000

6	6.402665000	-2.236871000	1.329345000
1	6.200516000	-2.835298000	2.216636000
1	7.129555000	-2.774240000	0.713055000
1	6.880611000	-1.303778000	1.636432000
6	6.562297000	-0.361037000	-0.825701000
1	6.687607000	0.358269000	-0.015696000
1	7.408945000	-1.046928000	-0.816394000
1	6.588590000	0.185788000	-1.770061000



Biradical species C-1



SOMO-1 SOMO-2

Charge = 2 Multiplicity = 3

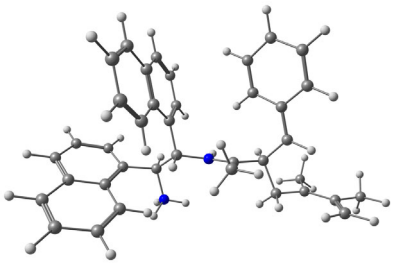
Sum of electronic and thermal Free Energies= -1580.226100

6	-1.652562000	-1.519892000	-1.548235000
1	-1.469625000	-1.204289000	-2.576726000
6	-0.789072000	-0.651650000	-0.611709000
1	-0.965822000	-0.940489000	0.416609000
6	-1.149713000	0.810257000	-0.818016000
6	-0.846463000	1.397540000	-2.024758000
6	-1.805845000	1.555436000	0.208141000

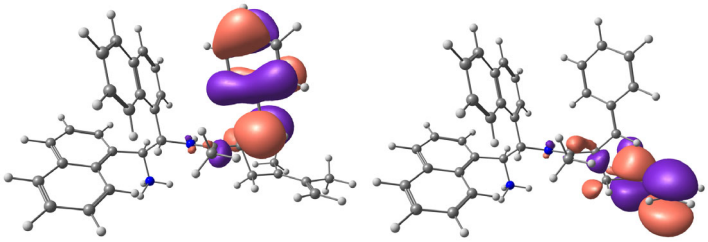
6	-1.156132000	2.748031000	-2.280252000
6	-2.115786000	2.921785000	-0.060892000
6	-1.775765000	3.491585000	-1.312464000
1	-0.363012000	0.828922000	-2.815382000
1	-0.905481000	3.183933000	-3.238986000
6	-3.123752000	-1.380763000	-1.244492000
6	-3.689925000	-1.818032000	-0.001499000
6	-3.906997000	-0.758793000	-2.187443000
6	-5.080721000	-1.586156000	0.205541000
6	-5.279361000	-0.528855000	-1.966679000
6	-5.849134000	-0.935942000	-0.793575000
1	-3.462462000	-0.422279000	-3.117994000
1	-5.867382000	-0.031565000	-2.726612000
6	-2.184828000	1.018862000	1.469493000
6	-2.827812000	1.792975000	2.398671000
6	-2.776279000	3.696098000	0.927665000
6	-3.126725000	3.147697000	2.129768000
1	-3.114262000	1.360764000	3.349748000
1	-3.002453000	4.732893000	0.706137000
1	-3.634806000	3.743947000	2.876977000
6	-2.973581000	-2.467984000	1.045728000
6	-5.692173000	-1.996620000	1.417569000
6	-3.595737000	-2.858131000	2.204894000
6	-4.972104000	-2.621614000	2.398280000
1	-6.750473000	-1.802877000	1.549879000
1	-3.022699000	-3.348749000	2.982221000
1	-5.448812000	-2.933200000	3.318699000
7	0.658499000	-0.849680000	-0.855438000
7	-1.250880000	-2.993213000	-1.526804000
1	-1.691739000	-3.492620000	-0.746431000
1	-0.236639000	-3.132330000	-1.467472000
6	1.594471000	-0.778319000	0.051924000
6	1.245100000	-0.692866000	1.495171000
1	2.146537000	-0.730220000	2.102386000

1	0.744788000	0.266066000	1.682336000
1	0.566897000	-1.495814000	1.795862000
6	3.026705000	-0.760397000	-0.375921000
1	3.073441000	-0.596101000	-1.461387000
6	3.756940000	0.331557000	0.351883000
1	4.564263000	0.030979000	1.010046000
6	3.418380000	1.704882000	0.264200000
6	2.399630000	2.200256000	-0.587708000
6	4.116034000	2.640337000	1.068151000
6	2.089954000	3.547824000	-0.616687000
6	3.802277000	3.985105000	1.028741000
6	2.784888000	4.447633000	0.191872000
1	1.860370000	1.532604000	-1.250262000
1	4.903810000	2.283827000	1.722165000
1	1.306714000	3.903017000	-1.275625000
1	4.348568000	4.682327000	1.651769000
1	2.540340000	5.502064000	0.165891000
1	-6.903193000	-0.767861000	-0.605045000
1	-1.905950000	-2.653331000	0.987593000
1	-2.023314000	4.531640000	-1.493420000
1	-1.991821000	-0.017190000	1.718652000
1	-1.578577000	-3.449145000	-2.384553000
1	0.969610000	-0.797455000	-1.824477000
6	5.822366000	-2.317195000	1.948863000
6	6.093062000	-2.269129000	0.600466000
6	5.099906000	-2.200289000	-0.397202000
6	3.637239000	-2.176654000	-0.079660000
1	3.115583000	-2.900818000	-0.715765000
1	6.632497000	-2.375128000	2.663639000
1	4.822088000	-2.303374000	2.360505000
1	3.440084000	-2.449194000	0.956672000
6	7.542174000	-2.276770000	0.162162000
1	8.203761000	-2.267270000	1.026638000
1	7.770517000	-3.166772000	-0.429171000

1	7.772908000	-1.404791000	-0.454189000
6	5.452239000	-2.024237000	-1.844311000
1	5.668086000	-0.971372000	-2.073611000
1	6.337879000	-2.595400000	-2.124153000
1	4.631061000	-2.338533000	-2.493541000



Biradidal open Shell singlet



Alpha HOMO Beta HOMO

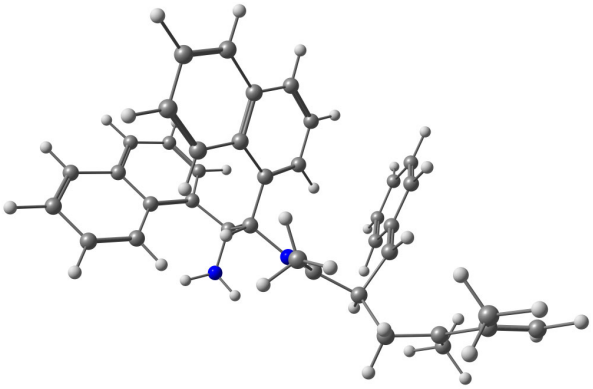
Charge = 2 Multiplicity = 1

Sum of electronic and thermal Free Energies= -1580.227142

6	-1.648839000	-1.545696000	-1.530353000
1	-1.468452000	-1.241773000	-2.562820000
6	-0.785009000	-0.663832000	-0.606526000
1	-0.960451000	-0.935870000	0.426692000
6	-1.148134000	0.794042000	-0.838120000
6	-0.843287000	1.360410000	-2.054443000
6	-1.812333000	1.554537000	0.171398000
6	-1.161414000	2.703503000	-2.337570000
6	-2.132818000	2.912774000	-0.126394000
6	-1.792567000	3.460287000	-1.387709000
1	-0.352645000	0.781003000	-2.832519000
1	-0.908928000	3.122653000	-3.303179000
6	-3.119296000	-1.402949000	-1.224725000

6	-3.681603000	-1.824823000	0.025247000
6	-3.904724000	-0.790638000	-2.172169000
6	-5.071252000	-1.588633000	0.234477000
6	-5.275953000	-0.556242000	-1.949282000
6	-5.842105000	-0.948769000	-0.769429000
1	-3.462624000	-0.465131000	-3.107804000
1	-5.866005000	-0.066782000	-2.712716000
6	-2.190006000	1.040828000	1.442450000
6	-2.841299000	1.828726000	2.354157000
6	-2.802686000	3.701565000	0.844110000
6	-3.151430000	3.174979000	2.056397000
1	-3.125706000	1.414244000	3.313658000
1	-3.037044000	4.731812000	0.601033000
1	-3.666178000	3.782282000	2.789969000
6	-2.962159000	-2.463234000	1.077339000
6	-5.678834000	-1.983745000	1.453509000
6	-3.580403000	-2.838105000	2.243662000
6	-4.955769000	-2.597392000	2.439211000
1	-6.736553000	-1.787583000	1.587213000
1	-3.005283000	-3.320346000	3.024681000
1	-5.429483000	-2.897083000	3.365112000
7	0.663338000	-0.861274000	-0.847955000
7	-1.248390000	-3.018914000	-1.493519000
1	-1.691738000	-3.510337000	-0.709429000
1	-0.234830000	-3.160919000	-1.431570000
6	1.599065000	-0.770552000	0.055246000
6	1.255271000	-0.664525000	1.497854000
1	2.160136000	-0.689085000	2.100776000
1	0.751122000	0.294623000	1.672582000
1	0.582153000	-1.466185000	1.812897000
6	3.033947000	-0.760735000	-0.376561000
1	3.075226000	-0.611192000	-1.464745000
6	3.783906000	0.329546000	0.333799000
1	4.617502000	0.031791000	0.958215000

6	3.423869000	1.699788000	0.272178000
6	2.378998000	2.189582000	-0.550220000
6	4.122678000	2.636091000	1.073778000
6	2.039315000	3.530754000	-0.547213000
6	3.780539000	3.974388000	1.065283000
6	2.733174000	4.430170000	0.261856000
1	1.845385000	1.524839000	-1.220096000
1	4.932648000	2.285200000	1.703260000
1	1.234868000	3.879846000	-1.183544000
1	4.327640000	4.672265000	1.686913000
1	2.466444000	5.479591000	0.260652000
1	-6.895131000	-0.776568000	-0.579064000
1	-1.895342000	-2.651811000	1.016232000
1	-2.048036000	4.494365000	-1.590381000
1	-1.987684000	0.012042000	1.713617000
1	-1.575710000	-3.482210000	-2.347453000
1	0.973474000	-0.829100000	-1.818536000
6	5.850499000	-2.267997000	1.939066000
6	6.110814000	-2.223362000	0.588873000
6	5.108983000	-2.173547000	-0.401812000
6	3.647759000	-2.169496000	-0.070620000
1	3.128006000	-2.907419000	-0.692255000
1	6.666726000	-2.301544000	2.648431000
1	4.853074000	-2.276326000	2.357378000
1	3.462812000	-2.430565000	0.970803000
6	7.555925000	-2.211223000	0.138235000
1	8.225015000	-2.175002000	0.996236000
1	7.795278000	-3.107225000	-0.439571000
1	7.765169000	-1.346510000	-0.495701000
6	5.449926000	-2.033382000	-1.856625000
1	5.686106000	-0.991556000	-2.111720000
1	6.320822000	-2.629690000	-2.131907000
1	4.617086000	-2.345964000	-2.491154000



(Transition state)

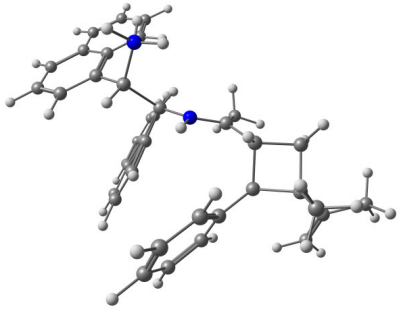
Charge = 2 Multiplicity = 1

Sum of electronic and thermal Free Energies= -1580.225661

6	-1.532057000	-0.325405000	-1.861348000
1	-1.076291000	0.522897000	-2.377321000
6	-0.714347000	-0.582783000	-0.577116000
1	-1.099719000	-1.460464000	-0.065141000
6	-0.832510000	0.654280000	0.304617000
6	-0.158728000	1.791864000	-0.070946000
6	-1.702015000	0.668689000	1.441003000
6	-0.311659000	3.001094000	0.639536000
6	-1.862058000	1.900436000	2.140659000
6	-1.153083000	3.052495000	1.715621000
1	0.504487000	1.787001000	-0.931995000
1	0.234046000	3.878705000	0.317375000
6	-2.978766000	-0.007231000	-1.578542000
6	-3.876588000	-0.977491000	-1.026390000
6	-3.397116000	1.281397000	-1.808160000
6	-5.204413000	-0.554119000	-0.731587000
6	-4.710877000	1.690287000	-1.504278000
6	-5.591490000	0.787965000	-0.977518000
1	-2.699199000	2.006487000	-2.213614000
1	-5.009614000	2.713713000	-1.688672000

6	-2.421996000	-0.462621000	1.912708000
6	-3.258239000	-0.368397000	2.994051000
6	-2.734414000	1.963306000	3.257484000
6	-3.424357000	0.858321000	3.673513000
1	-3.798401000	-1.245371000	3.330061000
1	-2.844066000	2.910132000	3.773880000
1	-4.091072000	0.916121000	4.524649000
6	-3.541069000	-2.332054000	-0.734214000
6	-6.131908000	-1.473438000	-0.177975000
6	-4.461690000	-3.196759000	-0.199256000
6	-5.775472000	-2.768204000	0.081887000
1	-7.135153000	-1.123903000	0.037340000
1	-4.175112000	-4.218715000	0.017250000
1	-6.490581000	-3.462819000	0.503539000
7	0.686105000	-0.884833000	-0.934760000
7	-1.447919000	-1.474628000	-2.867403000
1	-2.139593000	-2.202185000	-2.655026000
1	-0.522693000	-1.913960000	-2.909807000
6	1.572028000	-1.411054000	-0.110833000
6	1.116091000	-1.941435000	1.202882000
1	1.955106000	-2.144872000	1.861206000
1	0.433996000	-1.246025000	1.697720000
1	0.581213000	-2.884712000	1.038254000
6	3.012241000	-1.353180000	-0.504865000
1	3.089743000	-1.276910000	-1.589996000
6	3.349306000	-0.038739000	0.156649000
1	3.555581000	-0.073927000	1.220603000
6	3.209954000	1.232502000	-0.466304000
6	3.014680000	1.391375000	-1.859576000
6	3.262071000	2.398567000	0.332975000
6	2.839269000	2.650617000	-2.411003000
6	3.090869000	3.650621000	-0.226875000
6	2.864067000	3.783834000	-1.597970000
1	3.054530000	0.534937000	-2.523851000

1	3.428070000	2.297154000	1.399425000
1	2.707046000	2.757187000	-3.480937000
1	3.130225000	4.531129000	0.402778000
1	2.732491000	4.766170000	-2.034504000
1	-6.605594000	1.084354000	-0.734895000
1	-2.538263000	-2.723345000	-0.875687000
1	-1.291788000	3.978448000	2.262359000
1	-2.330553000	-1.425673000	1.428724000
1	-1.673575000	-1.123493000	-3.803126000
1	1.064920000	-0.417596000	-1.755413000
6	7.409461000	-1.026744000	1.003685000
6	6.164610000	-1.585329000	1.094839000
6	5.354733000	-1.743591000	-0.058103000
6	3.995635000	-2.411017000	-0.000917000
1	3.960708000	-3.309907000	-0.626478000
1	8.021342000	-0.894062000	1.886485000
1	7.829648000	-0.697984000	0.062447000
1	3.756675000	-2.712899000	1.017244000
6	5.660853000	-2.031259000	2.451629000
1	6.415590000	-1.844187000	3.213890000
1	4.755034000	-1.494555000	2.748435000
1	5.434803000	-3.100053000	2.463692000
6	5.879629000	-1.382645000	-1.418334000
1	6.134734000	-0.320468000	-1.485342000
1	6.790093000	-1.947155000	-1.643829000
1	5.160023000	-1.607902000	-2.206338000



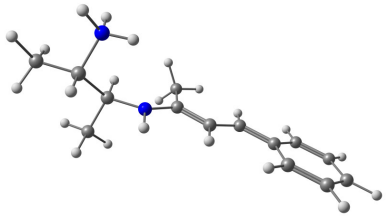
Charge = 2 Multiplicity = 1

Sum of electronic and thermal Free Energies= -1580.290615

6	-1.593961000	-0.565303000	-1.847810000
1	-1.145409000	0.187226000	-2.500405000
6	-0.738467000	-0.645969000	-0.563241000
1	-1.123833000	-1.420186000	0.090550000
6	-0.802099000	0.712299000	0.123226000
6	-0.133972000	1.770959000	-0.445954000
6	-1.637167000	0.909946000	1.268673000
6	-0.278941000	3.080028000	0.059901000
6	-1.775695000	2.237906000	1.768514000
6	-1.091977000	3.306119000	1.135059000
1	0.519447000	1.632528000	-1.305322000
1	0.249385000	3.894685000	-0.417749000
6	-3.024797000	-0.184700000	-1.559321000
6	-3.908368000	-1.056654000	-0.844074000
6	-3.441861000	1.064204000	-1.952311000
6	-5.225147000	-0.585441000	-0.575402000
6	-4.742338000	1.525010000	-1.666991000
6	-5.612376000	0.712592000	-0.995522000
1	-2.752907000	1.718336000	-2.475385000
1	-5.040653000	2.516107000	-1.982089000
6	-2.336958000	-0.128990000	1.941441000
6	-3.131196000	0.139641000	3.025222000
6	-2.604563000	2.481437000	2.893349000
6	-3.273844000	1.459155000	3.507098000

1	-3.653561000	-0.670579000	3.519587000
1	-2.694685000	3.498449000	3.257316000
1	-3.906526000	1.654825000	4.363615000
6	-3.567730000	-2.355840000	-0.367317000
6	-6.138522000	-1.409719000	0.130089000
6	-4.475104000	-3.130771000	0.309618000
6	-5.779729000	-2.657975000	0.560407000
1	-7.133776000	-1.025214000	0.322754000
1	-4.183235000	-4.111874000	0.663705000
1	-6.485283000	-3.280028000	1.095683000
7	0.651362000	-1.024265000	-0.887523000
7	-1.574872000	-1.852850000	-2.675014000
1	-2.289624000	-2.514021000	-2.350102000
1	-0.670263000	-2.333726000	-2.671082000
6	1.476727000	-1.633156000	-0.077192000
6	0.997926000	-2.116752000	1.244139000
1	1.823440000	-2.482273000	1.846447000
1	0.487568000	-1.310507000	1.780680000
1	0.283732000	-2.935463000	1.105751000
6	2.891607000	-1.651980000	-0.473099000
1	2.979249000	-1.618954000	-1.558958000
6	3.618581000	-0.395918000	0.145780000
1	3.304006000	-0.299756000	1.189706000
6	3.440523000	0.924858000	-0.543661000
6	3.420517000	1.049769000	-1.937642000
6	3.252197000	2.073966000	0.228633000
6	3.228906000	2.290719000	-2.538526000
6	3.077732000	3.316343000	-0.368952000
6	3.060573000	3.428341000	-1.755233000
1	3.581538000	0.186209000	-2.573473000
1	3.238531000	1.996513000	1.310813000
1	3.231501000	2.371102000	-3.618877000
1	2.948701000	4.195965000	0.250203000
1	2.925999000	4.396237000	-2.222803000

1	-6.617334000	1.049644000	-0.769138000
1	-2.566940000	-2.762636000	-0.475022000
1	-1.224301000	4.309232000	1.524636000
1	-2.263099000	-1.158481000	1.616272000
1	-1.806391000	-1.633931000	-3.648758000
1	1.071600000	-0.600963000	-1.716043000
6	5.823284000	-0.028763000	2.113800000
6	5.808370000	-1.133416000	1.373887000
6	4.922177000	-1.270131000	0.157450000
6	3.999826000	-2.528317000	0.134015000
1	4.321028000	-3.375256000	-0.471000000
1	6.483458000	0.062870000	2.968289000
1	5.202721000	0.829324000	1.881293000
1	3.770712000	-2.865043000	1.145486000
6	6.701464000	-2.310721000	1.665266000
1	7.219779000	-2.175895000	2.613958000
1	6.130118000	-3.242430000	1.715550000
1	7.456007000	-2.438282000	0.884757000
6	5.745362000	-1.148376000	-1.125055000
1	6.160338000	-0.142938000	-1.216905000
1	6.569814000	-1.862805000	-1.104794000
1	5.157947000	-1.364602000	-2.020992000



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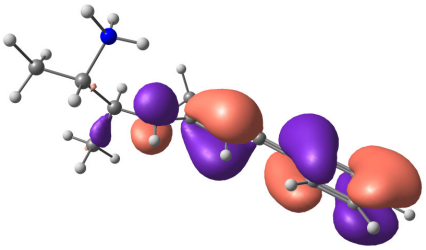
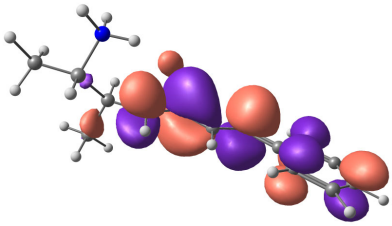
Sum of electronic and thermal Free Energies= -655.385341





HOMO LUMO

6	4.084103000	-0.808574000	-0.160184000
1	3.867539000	-1.783922000	0.283238000
6	3.164977000	0.263235000	0.441854000
1	3.295405000	1.189621000	-0.119994000
7	1.762830000	-0.161406000	0.295902000
7	3.750087000	-0.965533000	-1.633300000
1	3.988840000	-0.120219000	-2.162963000
1	2.753491000	-1.155796000	-1.780695000
6	0.727878000	0.590341000	-0.059416000
6	0.997960000	1.968748000	-0.567739000
1	0.090218000	2.486691000	-0.852508000
1	1.503693000	2.555188000	0.203322000
1	1.649496000	1.926731000	-1.444393000
6	-0.565538000	0.021641000	0.067764000
1	-0.610186000	-0.998527000	0.433131000
6	-1.724000000	0.688654000	-0.203415000
1	-1.674892000	1.721895000	-0.531860000
6	-3.059582000	0.165807000	-0.080297000

6	-3.333373000	-1.174423000	0.256064000
6	-4.130305000	1.047800000	-0.311005000
6	-4.640356000	-1.608084000	0.359217000
6	-5.439522000	0.609289000	-0.200411000
6	-5.693206000	-0.717318000	0.134184000
1	-2.528457000	-1.878522000	0.427156000
1	-3.923503000	2.080192000	-0.571122000
1	-4.850419000	-2.639246000	0.613184000
1	-6.258620000	1.294505000	-0.375498000
1	-6.715517000	-1.065543000	0.217793000
1	4.275403000	-1.741494000	-2.048771000
1	1.538279000	-1.048716000	0.741063000
6	3.475627000	0.522262000	1.915708000
1	3.437633000	-0.403786000	2.493154000
1	4.462589000	0.968738000	2.027744000
1	2.741768000	1.218325000	2.322504000
6	5.561577000	-0.484153000	-0.022741000
1	6.170356000	-1.198400000	-0.577840000
1	5.784484000	0.525662000	-0.375712000
1	5.854536000	-0.556151000	1.023336000

TDDFT (CAMB3LYP/631G*) transitions analysis (Excitation energies and oscillator strengths):

Excited State 1: Triplet **2.0001 eV** 619.89 nm f=0.0000 <S**2>=2.000

57 -> 60 -0.16149

58 -> 63 0.10670

59 -> 60 0.67961

59 -> 61 0.10384

59 <- 60 0.13800

Excited State 2: Triplet 3.0891 eV 401.36 nm f=0.0000 <S**2>=2.000

58 -> 60 0.66608

58 -> 61 0.20536

Excited State 3: Singlet 3.5136 eV **352.87 nm f=1.1975** <S**2>=0.000

59 -> 60 0.69694 (HOMO-LUMO transition)

Excited State 4: Triplet 3.7540 eV 330.27 nm f=0.0000 <S**2>=2.000

52 -> 60 0.13044

57 -> 60 0.52162

58 -> 63 0.26248

59 -> 61 0.28285

59 -> 62 -0.13527

59 -> 67 -0.10762

Excited State 5: Singlet 3.8169 eV 324.83 nm f=0.0463 <S**2>=0.000

58 -> 60 0.69103

Excited State 6: Triplet 4.3469 eV 285.23 nm f=0.0000 <S**2>=2.000

57 -> 60 -0.33272

58 -> 61 -0.12930

58 -> 62 0.14211

58 -> 63 0.55104

59 -> 60 -0.18278

Excited State 7: Triplet 5.1476 eV 240.86 nm f=0.0000 <S**2>=2.000

52 -> 60 -0.11416

57 -> 60 -0.16934

57 -> 67 -0.15618

58 -> 63 -0.21388

59 -> 60 -0.10094

59 -> 61 0.52852

59 -> 62 -0.23520

Excited State 8: Triplet 5.3888 eV 230.08 nm f=0.0000 <S**2>=2.000

57 -> 63 0.19958

58 -> 61 0.11600

59 -> 62 0.10221

59 -> 63 0.63879

Excited State 9: Singlet 5.7848 eV 214.33 nm f=0.1499 <S**2>=0.000

56 -> 60 0.12362

57 -> 60 0.66342

58 -> 63 0.13998

Excited State 10: Singlet 5.9220 eV 209.36 nm f=0.0052 <S**2>=0.000

56 -> 60 0.65108

56 -> 61 0.14134

57 -> 60 -0.12384

Excited State 11: Singlet 6.0739 eV 204.13 nm f=0.0132 <S**2>=0.000

57 -> 63 0.10011

58 -> 60 0.13560

58 -> 61 -0.32598

58 -> 62 0.13787

58 -> 63 -0.13728

58 -> 67 0.14445

59 -> 61 -0.23839

59 -> 62 0.16807

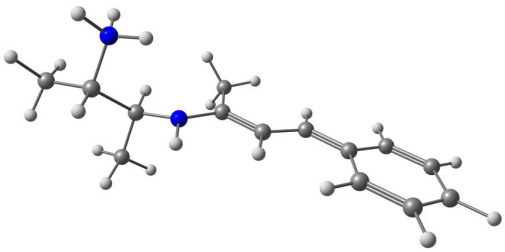
59 -> 63 0.45827

Excited State 12: Singlet 6.1923 eV 200.22 nm f=0.0012 <S**2>=0.000

51 -> 60 -0.14759

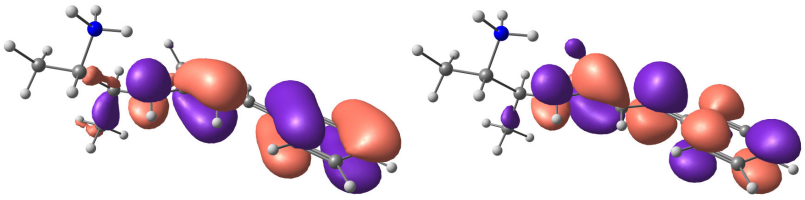
55 -> 60 0.65164

55 -> 61 0.13524



Charge = 2 Multiplicity = 3

Sum of electronic and thermal Free Energies= -655.307038



SOMO1 SOMO2

6 4.109189000 -0.767961000 -0.249733000

1	3.890839000	-1.810403000	-0.002905000
6	3.133171000	0.153930000	0.491592000
1	3.278880000	1.176587000	0.138353000
7	1.759235000	-0.239183000	0.156006000
7	3.842227000	-0.647445000	-1.737535000
1	4.167236000	0.255133000	-2.098545000
1	2.839417000	-0.723562000	-1.940603000
6	0.725671000	0.621487000	-0.046061000
6	1.029827000	2.055817000	-0.331609000
1	0.138995000	2.591105000	-0.644606000
1	1.430146000	2.554067000	0.556649000
1	1.769731000	2.148949000	-1.131311000
6	-0.578764000	0.093627000	0.019121000
1	-0.644874000	-0.974501000	0.205131000
6	-1.778644000	0.819267000	-0.115616000
1	-1.740373000	1.891982000	-0.250583000
6	-3.050022000	0.230892000	-0.060674000
6	-3.283181000	-1.187414000	0.107206000
6	-4.210435000	1.085943000	-0.174088000
6	-4.553737000	-1.683123000	0.163606000
6	-5.470717000	0.573801000	-0.114501000
6	-5.666689000	-0.820196000	0.056400000
1	-2.449592000	-1.870632000	0.190056000
1	-4.052284000	2.149785000	-0.302560000
1	-4.716065000	-2.745647000	0.291453000
1	-6.330262000	1.226893000	-0.194504000
1	-6.669767000	-1.223105000	0.103559000
1	4.330077000	-1.378462000	-2.262830000
1	1.502544000	-1.173677000	0.461711000
6	3.355514000	0.105075000	2.004302000
1	3.334376000	-0.924634000	2.370268000
1	4.315535000	0.549368000	2.265670000
1	2.571476000	0.671835000	2.506388000
6	5.571558000	-0.454018000	0.009759000

1	6.218294000	-1.054580000	-0.631450000
1	5.788092000	0.604253000	-0.158011000
1	5.820896000	-0.697116000	1.041154000

13. X-Ray Crystallographic Data for 5a

A clear colorless plate-like specimen of $C_{23}H_{28}N_2O_2S$, approximate dimensions 0.018 mm x 0.084mm x 0.279 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured.

The total exposure time was 19.08 hours. The frames were integrated with the Bruker SAINT[1] software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 38086 reflections to a maximum θ angle of 25.36° (0.83 Å resolution), of which 8169 were independent (average redundancy 4.662, completeness = 100.0%, R_{int} = 6.88%, R_{sig} = 7.96%) and 4763 (58.31%) were greater than $2\sigma(F^2)$. The final cell constants of a = 7.7639(11) Å, b = 9.7745(15)Å, c = 16.044(3) Å, α = 90.123(7)°, β = 96.248(6)°, γ = 112.826(6)°, volume = 1114.2(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 4681 reflections above 20 σ(I) with 5.088° < 2θ < 39.47°. Data were corrected for absorption effects using the multi-scan method (SADABS).[2] The ratio of minimum to maximum apparent transmission was 0.905. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9550 and 0.9970.

The structure was solved and refined using the Bruker SHELXTL[3] Software Package, using the space group P 1, with Z = 2 for the formula unit, $C_{23}H_{28}N_2O_2S$. The final anisotropic full-matrix least-squares refinement on F^2 with 513 variables converged at R1 = 5.17%, for the observed data and wR2 = 14.30% for all data. The goodness-of-fit was 1.017. The largest peak in the final difference electron density synthesis was 0.228 $e^-/Å^3$ and the largest hole was -0.333 $e^-/Å^3$ with an RMS deviation of 0.074 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.182 g/cm^3 and F(000), 424 e^-.

Table S5. Sample and crystal data

Identification code	**5a**
Chemical formula	$C_{23}H_{28}N_2O_2S$
Formula weight	396.53 g/mol
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal size	0.018 x 0.084 x 0.279 mm

Crystal habit	clear colourless plate	
Crystal system	triclinic	
Space group	P 1	
Unit cell dimensions	a = 7.7639(11) Å	α = 90.123(7)°
	b = 9.7745(15) Å	β = 96.248(6)°
	c = 16.044(3) Å	γ = 112.826(6)°
Volume	1114.2(3) $Å^3$	
Z	2	
Density (calculated)	1.182 g/cm^3	
Absorption coefficient	0.165 mm^{-1}	
F(000)	424	

Table S6. Data collection and structure refinement

Theta range for data collection	1.28 to 25.36°
Index ranges	-9<=h<=9, -11<=k<=11, -19<=l<=19
Reflections collected	38086
Independent reflections	8169 [R(int) = 0.0688]
Coverage of independent reflections	100.0%
Absorption correction	multi-scan
Max. and min. transmission	0.9970 and 0.9550
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick 2008)
Refinement method	Full-matrix least-squares on F^2

Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8169 / 3 / 513
Goodness-of-fit on F^2	1.017
Δ/σ_{max}	0.001
Final R indices	4763 data; $I>2\sigma(I)$ R1 = 0.0517, wR2 = 0.1085
	all data R1 = 0.1243, wR2 = 0.1430
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0723P)^2]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	-0.0(0)
Largest diff. peak and hole	0.228 and -0.333 eÅ^{-3}
R.M.S. deviation from mean	0.074 eÅ^{-3}

Table S7. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1	0.4727(9)	0.1847(8)	0.4048(4)	0.0476(17)
C2	0.4223(10)	0.1597(8)	0.4846(5)	0.063(2)
C3	0.3018(11)	0.0207(10)	0.5027(6)	0.074(2)
C4	0.2312(10)	0.9048(9)	0.4444(7)	0.067(2)
C5	0.2846(12)	0.9333(9)	0.3657(6)	0.077(2)

	x/a	y/b	z/c	U(eq)
C6	0.4030(11)	0.0693(8)	0.3455(5)	0.064(2)
C7	0.0964(12)	0.7558(9)	0.4669(8)	0.111(4)
C8	0.2193(9)	0.4059(7)	0.2399(4)	0.0445(16)
C9	0.1719(9)	0.5189(7)	0.2831(4)	0.0561(18)
C10	0.1089(8)	0.3271(7)	0.1598(4)	0.0487(17)
C11	0.8926(7)	0.2366(6)	0.1555(3)	0.0448(14)
C12	0.8709(9)	0.2882(7)	0.0630(4)	0.0560(17)
C13	0.0674(9)	0.4163(8)	0.0879(4)	0.0602(19)
C14	0.8130(9)	0.0762(7)	0.1734(4)	0.0494(16)
C15	0.9172(11)	0.0035(8)	0.2116(4)	0.065(2)
C16	0.8379(13)	0.8549(9)	0.2273(5)	0.081(2)
C17	0.6489(14)	0.7753(9)	0.2045(5)	0.079(3)
C18	0.5411(12)	0.8465(9)	0.1677(5)	0.087(3)
C19	0.6217(10)	0.9929(8)	0.1527(5)	0.076(2)
C20	0.8889(13)	0.1785(9)	0.9987(5)	0.088(2)
C21	0.7063(10)	0.3298(8)	0.0400(5)	0.069(2)
C22	0.6713(13)	0.4309(11)	0.0996(5)	0.103(3)
C23	0.5935(15)	0.2828(11)	0.9678(7)	0.123(4)
C24	0.6519(8)	0.8213(7)	0.5453(4)	0.0424(16)
C25	0.7577(11)	0.9347(8)	0.6037(5)	0.063(2)
C26	0.8748(11)	0.0696(8)	0.5768(6)	0.073(2)
C27	0.8857(10)	0.0923(8)	0.4922(6)	0.060(2)
C28	0.7807(10)	0.9788(8)	0.4353(5)	0.063(2)
C29	0.6645(9)	0.8423(8)	0.4622(5)	0.0570(19)
C30	0.0157(12)	0.2408(9)	0.4641(7)	0.095(3)
C31	0.9233(10)	0.5956(7)	0.6933(4)	0.0476(17)

	x/a	y/b	z/c	U(eq)
C32	0.9375(11)	0.4629(8)	0.6534(5)	0.064(2)
C33	0.0694(9)	0.6759(7)	0.7646(4)	0.0520(17)
C34	0.0671(9)	0.8177(6)	0.8046(4)	0.0518(16)
C35	0.1124(10)	0.7635(7)	0.8943(4)	0.0631(18)
C36	0.0414(11)	0.6058(8)	0.8513(5)	0.067(2)
C37	0.1857(11)	0.9701(8)	0.7815(4)	0.065(2)
C38	0.1347(13)	0.0865(9)	0.8013(5)	0.091(3)
C39	0.245(2)	0.2308(12)	0.7836(8)	0.128(4)
C40	0.397(3)	0.2541(15)	0.7441(8)	0.155(7)
C41	0.450(2)	0.1463(16)	0.7229(7)	0.155(6)
C42	0.3465(14)	0.0005(10)	0.7433(6)	0.108(3)
C43	0.3215(11)	0.8179(11)	0.9210(5)	0.096(3)
C44	0.0048(14)	0.7873(9)	0.9607(5)	0.086(2)
C45	0.7920(16)	0.7303(13)	0.9409(7)	0.138(4)
C46	0.089(2)	0.8604(15)	0.0327(7)	0.158(5)
N1	0.4679(6)	0.4398(5)	0.3416(3)	0.0444(13)
N2	0.3561(8)	0.3681(6)	0.2672(3)	0.0481(14)
N3	0.6527(7)	0.5629(6)	0.6086(4)	0.0526(15)
N4	0.7939(7)	0.6424(6)	0.6740(3)	0.0458(14)
O1	0.7139(6)	0.3515(6)	0.3116(3)	0.0721(15)
O2	0.7125(6)	0.4505(5)	0.4531(3)	0.0614(14)
O3	0.3943(6)	0.5582(5)	0.5079(3)	0.0642(14)
O4	0.4310(6)	0.6682(6)	0.6505(3)	0.0726(15)
S1	0.61183(18)	0.36288(16)	0.37771(10)	0.0500(5)
S2	0.5112(2)	0.64712(17)	0.57868(11)	0.0538(5)

Table S8. Bond lengths (Å)

C1-C6	1.371(9)	C1-C2	1.373(9)
C1-S1	1.742(7)	C2-C3	1.371(10)
C2-H2	0.93	C3-C4	1.364(11)
C3-H3	0.93	C4-C5	1.368(12)
C4-C7	1.499(11)	C5-C6	1.356(11)
C5-H5	0.93	C6-H6	0.93
C7-H7A	0.96	C7-H7B	0.96
C7-H7C	0.96	C8-N2	1.289(8)
C8-C9	1.484(9)	C8-C10	1.490(8)
C9-H9A	0.96	C9-H9B	0.96
C9-H9C	0.96	C10-C13	1.529(9)
C10-C11	1.559(8)	C10-H10	0.98
C11-C14	1.487(8)	C11-C12	1.580(8)
C11-H11	0.98	C12-C21	1.496(10)
C12-C20	1.542(9)	C12-C13	1.561(9)
C13-H13A	0.97	C13-H13B	0.97
C14-C15	1.369(9)	C14-C19	1.390(9)
C15-C16	1.376(10)	C15-H15	0.93
C16-C17	1.375(11)	C16-H16	0.93
C17-C18	1.371(11)	C17-H17	0.93
C18-C19	1.355(10)	C18-H18	0.93
C19-H19	0.93	C20-H20A	0.96
C20-H20B	0.96	C20-H20C	0.96

C21-C23	1.335(10)	C21-C22	1.492(11)
C22-H22A	0.96	C22-H22B	0.96
C22-H22C	0.96	C23-H23A	0.93
C23-H23B	0.93	C24-C29	1.358(9)
C24-C25	1.379(9)	C24-S2	1.752(7)
C25-C26	1.382(11)	C25-H25	0.93
C26-C27	1.382(11)	C26-H26	0.93
C27-C28	1.364(10)	C27-C30	1.515(11)
C28-C29	1.390(10)	C28-H28	0.93
C29-H29	0.93	C30-H30A	0.96
C30-H30B	0.96	C30-H30C	0.96
C31-N4	1.266(8)	C31-C32	1.492(10)
C31-C33	1.495(9)	C32-H32A	0.96
C32-H32B	0.96	C32-H32C	0.96
C33-C34	1.533(9)	C33-C36	1.550(10)
C33-H33	0.98	C34-C37	1.489(9)
C34-C35	1.586(9)	C34-H34	0.98
C35-C44	1.493(10)	C35-C43	1.509(10)
C35-C36	1.553(10)	C36-H36A	0.97
C36-H36B	0.97	C37-C42	1.379(11)
C37-C38	1.388(11)	C38-C39	1.386(14)

C38-H38	0.93	C39-C40	1.342(19)
C39-H39	0.93	C40-C41	1.33(2)
C40-H40	0.93	C41-C42	1.398(14)
C41-H41	0.93	C42-H42	0.93
C43-H43A	0.96	C43-H43B	0.96
C43-H43C	0.96	C44-C46	1.320(13)
C44-C45	1.521(13)	C45-H45A	0.96
C45-H45B	0.96	C45-H45C	0.96
C46-H46A	0.93	C46-H46B	0.93
N1-N2	1.402(7)	N1-S1	1.632(5)
N1-H1N	0.86	N3-N4	1.411(7)
N3-S2	1.644(6)	N3-H3N	0.86
O1-S1	1.420(5)	O2-S1	1.441(5)
O3-S2	1.424(5)	O4-S2	1.419(5)

Table S9. Bond angles (°)

C6-C1-C2	119.1(7)	C6-C1-S1	120.3(6)
C2-C1-S1	120.4(6)	C3-C2-C1	119.3(7)
C3-C2-H2	120.3	C1-C2-H2	120.3
C4-C3-C2	122.3(8)	C4-C3-H3	118.8
C2-C3-H3	118.8	C3-C4-C5	116.9(8)
C3-C4-C7	120.2(9)	C5-C4-C7	122.8(9)
C6-C5-C4	122.4(8)	C6-C5-H5	118.8

C4-C5-H5	118.8	C5-C6-C1	120.0(8)
C5-C6-H6	120.0	C1-C6-H6	120.0
C4-C7-H7A	109.5	C4-C7-H7B	109.5
H7A-C7-H7B	109.5	C4-C7-H7C	109.5
H7A-C7-H7C	109.5	H7B-C7-H7C	109.5
N2-C8-C9	123.9(6)	N2-C8-C10	114.8(6)
C9-C8-C10	121.4(6)	C8-C9-H9A	109.5
C8-C9-H9B	109.5	H9A-C9-H9B	109.5
C8-C9-H9C	109.5	H9A-C9-H9C	109.5
H9B-C9-H9C	109.5	C8-C10-C13	119.6(6)
C8-C10-C11	120.3(5)	C13-C10-C11	87.8(5)
C8-C10-H10	109.1	C13-C10-H10	109.1
C11-C10-H10	109.1	C14-C11-C10	121.7(5)
C14-C11-C12	120.5(5)	C10-C11-C12	88.5(4)
C14-C11-H11	108.1	C10-C11-H11	108.1
C12-C11-H11	108.1	C21-C12-C20	113.6(6)
C21-C12-C13	117.8(6)	C20-C12-C13	109.6(6)
C21-C12-C11	116.0(5)	C20-C12-C11	110.9(6)
C13-C12-C11	85.9(4)	C10-C13-C12	90.3(5)
C10-C13-H13A	113.6	C12-C13-H13A	113.6
C10-C13-H13B	113.6	C12-C13-H13B	113.6
H13A-C13-H13B	110.9	C15-C14-C19	116.6(6)
C15-C14-C11	123.7(6)	C19-C14-C11	119.7(6)
C14-C15-C16	121.9(7)	C14-C15-H15	119.0
C16-C15-H15	119.0	C15-C16-C17	119.9(8)

C15-C16-H16	120.1	C17-C16-H16	120.1
C18-C17-C16	119.2(7)	C18-C17-H17	120.4
C16-C17-H17	120.4	C19-C18-C17	120.1(8)
C19-C18-H18	120.0	C17-C18-H18	120.0
C18-C19-C14	122.4(8)	C18-C19-H19	118.8
C14-C19-H19	118.8	C12-C20-H20A	109.5
C12-C20-H20B	109.5	H20A-C20-H20B	109.5
C12-C20-H20C	109.5	H20A-C20-H20C	109.5
H20B-C20-H20C	109.5	C23-C21-C22	119.3(8)
C23-C21-C12	122.6(8)	C22-C21-C12	118.1(6)
C21-C22-H22A	109.5	C21-C22-H22B	109.5
H22A-C22-H22B	109.5	C21-C22-H22C	109.5
H22A-C22-H22C	109.5	H22B-C22-H22C	109.5
C21-C23-H23A	120.0	C21-C23-H23B	120.0
H23A-C23-H23B	120.0	C29-C24-C25	120.0(6)
C29-C24-S2	120.0(5)	C25-C24-S2	119.9(6)
C24-C25-C26	119.4(7)	C24-C25-H25	120.3
C26-C25-H25	120.3	C27-C26-C25	120.7(7)
C27-C26-H26	119.6	C25-C26-H26	119.6
C28-C27-C26	119.1(7)	C28-C27-C30	121.1(9)
C26-C27-C30	119.9(8)	C27-C28-C29	120.4(7)

C27-C28-H28	119.8	C29-C28-H28	119.8
C24-C29-C28	120.3(7)	C24-C29-H29	119.8
C28-C29-H29	119.8	C27-C30-H30A	109.5
C27-C30-H30B	109.5	H30A-C30-H30B	109.5
C27-C30-H30C	109.5	H30A-C30-H30C	109.5
H30B-C30-H30C	109.5	N4-C31-C32	125.5(6)
N4-C31-C33	117.2(6)	C32-C31-C33	117.2(6)
C31-C32-H32A	109.5	C31-C32-H32B	109.5
H32A-C32-H32B	109.5	C31-C32-H32C	109.5
H32A-C32-H32C	109.5	H32B-C32-H32C	109.5
C31-C33-C34	119.1(6)	C31-C33-C36	116.4(6)
C34-C33-C36	88.3(5)	C31-C33-H33	110.4
C34-C33-H33	110.4	C36-C33-H33	110.4
C37-C34-C33	123.5(6)	C37-C34-C35	119.1(5)
C33-C34-C35	89.1(5)	C37-C34-H34	107.8
C33-C34-H34	107.8	C35-C34-H34	107.8
C44-C35-C43	113.6(7)	C44-C35-C36	117.7(6)
C43-C35-C36	109.4(6)	C44-C35-C34	115.1(6)
C43-C35-C34	111.9(6)	C36-C35-C34	86.3(5)
C35-C36-C33	89.8(5)	C35-C36-H36A	113.7
C33-C36-H36A	113.7	C35-C36-H36B	113.7

C33-C36-H36B	113.7	H36A-C36-H36B	110.9
C42-C37-C38	118.9(8)	C42-C37-C34	122.6(8)
C38-C37-C34	118.5(7)	C39-C38-C37	120.3(11)
C39-C38-H38	119.8	C37-C38-H38	119.8
C40-C39-C38	118.5(13)	C40-C39-H39	120.7
C38-C39-H39	120.7	C41-C40-C39	123.4(13)
C41-C40-H40	118.3	C39-C40-H40	118.3
C40-C41-C42	119.4(13)	C40-C41-H41	120.3
C42-C41-H41	120.3	C37-C42-C41	119.4(11)
C37-C42-H42	120.3	C41-C42-H42	120.3
C35-C43-H43A	109.5	C35-C43-H43B	109.5
H43A-C43-H43B	109.5	C35-C43-H43C	109.5
H43A-C43-H43C	109.5	H43B-C43-H43C	109.5
C46-C44-C35	122.2(10)	C46-C44-C45	120.4(10)
C35-C44-C45	117.4(7)	C44-C45-H45A	109.5
C44-C45-H45B	109.5	H45A-C45-H45B	109.5
C44-C45-H45C	109.5	H45A-C45-H45C	109.5
H45B-C45-H45C	109.5	C44-C46-H46A	120.0
C44-C46-H46B	120.0	H46A-C46-H46B	120.0
N2-N1-S1	112.8(4)	N2-N1-H1N	123.6
S1-N1-H1N	123.6	C8-N2-N1	117.8(5)

N4-N3-S2	113.0(4)	N4-N3-H3N	123.5
S2-N3-H3N	123.5	C31-N4-N3	117.0(6)
O1-S1-O2	119.3(3)	O1-S1-N1	107.8(3)
O2-S1-N1	104.6(3)	O1-S1-C1	108.9(3)
O2-S1-C1	108.9(3)	N1-S1-C1	106.6(3)
O4-S2-O3	120.3(3)	O4-S2-N3	107.2(3)
O3-S2-N3	104.0(3)	O4-S2-C24	108.8(3)
O3-S2-C24	109.0(3)	N3-S2-C24	106.8(3)

Table S10. Torsion angles (°)

C6-C1-C2-C3	-0.8(10)	S1-C1-C2-C3	175.4(6)
C1-C2-C3-C4	0.8(12)	C2-C3-C4-C5	-0.6(12)
C2-C3-C4-C7	-178.6(7)	C3-C4-C5-C6	0.4(12)
C7-C4-C5-C6	178.3(7)	C4-C5-C6-C1	-0.5(12)
C2-C1-C6-C5	0.6(10)	S1-C1-C6-C5	-175.6(6)
N2-C8-C10-C13	-131.0(6)	C9-C8-C10-C13	48.8(8)
N2-C8-C10-C11	122.7(6)	C9-C8-C10-C11	-57.4(8)
C8-C10-C11-C14	-90.5(7)	C13-C10-C11-C14	146.1(6)
C8-C10-C11-C12	144.0(6)	C13-C10-C11-C12	20.6(5)
C14-C11-C12-C21	94.3(7)	C10-C11-C12-C21	-139.2(6)
C14-C11-C12-C20	-37.3(8)	C10-C11-C12-C20	89.2(6)

C14-C11-C12-C13	-146.7(6)	C10-C11-C12-C13	-20.2(5)
C8-C10-C13-C12	-144.8(5)	C11-C10-C13-C12	-20.9(5)
C21-C12-C13-C10	137.9(6)	C20-C12-C13-C10	-90.2(6)
C11-C12-C13-C10	20.6(5)	C10-C11-C14-C15	14.5(9)
C12-C11-C14-C15	123.7(7)	C10-C11-C14-C19	-167.1(6)
C12-C11-C14-C19	-57.9(8)	C19-C14-C15-C16	1.3(10)
C11-C14-C15-C16	179.7(6)	C14-C15-C16-C17	-0.1(11)
C15-C16-C17-C18	-1.2(12)	C16-C17-C18-C19	1.2(12)
C17-C18-C19-C14	0.1(12)	C15-C14-C19-C18	-1.3(11)
C11-C14-C19-C18	-179.8(7)	C20-C12-C21-C23	-3.9(10)
C13-C12-C21-C23	126.2(8)	C11-C12-C21-C23	-134.2(8)
C20-C12-C21-C22	177.7(6)	C13-C12-C21-C22	-52.2(8)
C11-C12-C21-C22	47.4(8)	C29-C24-C25-C26	0.6(10)
S2-C24-C25-C26	177.1(6)	C24-C25-C26-C27	0.5(11)
C25-C26-C27-C28	-0.8(11)	C25-C26-C27-C30	-179.7(7)
C26-C27-C28-C29	0.0(11)	C30-C27-C28-C29	178.9(6)
C25-C24-C29-C28	-1.4(10)	S2-C24-C29-C28	-177.8(5)

C27-C28-C29-C24	1.1(10)	N4-C31-C33-C34	-6.0(9)
C32-C31-C33-C34	176.7(6)	N4-C31-C33-C36	97.8(8)
C32-C31-C33-C36	-79.5(8)	C31-C33-C34-C37	-96.5(7)
C36-C33-C34-C37	144.1(7)	C31-C33-C34-C35	138.5(6)
C36-C33-C34-C35	19.1(5)	C37-C34-C35-C44	93.4(8)
C33-C34-C35-C44	-138.0(6)	C37-C34-C35-C43	-38.3(9)
C33-C34-C35-C43	90.3(6)	C37-C34-C35-C36	-147.7(7)
C33-C34-C35-C36	-19.1(5)	C44-C35-C36-C33	135.3(6)
C43-C35-C36-C33	-93.1(6)	C34-C35-C36-C33	18.8(5)
C31-C33-C36-C35	-141.4(6)	C34-C33-C36-C35	-19.5(5)
C33-C34-C37-C42	-20.9(10)	C35-C34-C37-C42	89.5(8)
C33-C34-C37-C38	160.9(6)	C35-C34-C37-C38	-88.7(8)
C42-C37-C38-C39	-0.6(12)	C34-C37-C38-C39	177.7(7)
C37-C38-C39-C40	2.6(15)	C38-C39-C40-C41	-2.(2)
C39-C40-C41-C42	-1.(2)	C38-C37-C42-C41	-2.2(13)
C34-C37-C42-C41	179.6(9)	C40-C41-C42-C37	3.1(19)
C43-C35-C44-C46	5.4(12)	C36-C35-C44-C46	135.0(9)

C34-C35-C44-C46	-125.5(9)	C43-C35-C44-C45	-177.6(8)
C36-C35-C44-C45	-48.0(10)	C34-C35-C44-C45	51.6(9)
C9-C8-N2-N1	-0.9(9)	C10-C8-N2-N1	178.9(5)
S1-N1-N2-C8	170.2(5)	C32-C31-N4-N3	-0.7(10)
C33-C31-N4-N3	-177.8(5)	S2-N3-N4-C31	-171.0(5)
N2-N1-S1-O1	52.2(5)	N2-N1-S1-O2	-179.9(4)
N2-N1-S1-C1	-64.6(5)	C6-C1-S1-O1	-30.8(6)
C2-C1-S1-O1	153.1(5)	C6-C1-S1-O2	-162.4(5)
C2-C1-S1-O2	21.5(6)	C6-C1-S1-N1	85.3(6)
C2-C1-S1-N1	-90.8(6)	N4-N3-S2-O4	-57.4(5)
N4-N3-S2-O3	174.2(4)	N4-N3-S2-C24	59.0(5)
C29-C24-S2-O4	-145.8(5)	C25-C24-S2-O4	37.8(6)
C29-C24-S2-O3	-12.9(6)	C25-C24-S2-O3	170.7(5)
C29-C24-S2-N3	98.8(6)	C25-C24-S2-N3	-77.6(6)

Table S11. Anisotropic atomic displacement parameters ($Å^2$)

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.042(4)	0.053(5)	0.054(4)	0.000(4)	0.002(3)	0.026(4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2	0.057(4)	0.058(5)	0.065(5)	0.004(4)	0.005(4)	0.014(4)
C3	0.067(5)	0.078(6)	0.080(6)	0.031(5)	0.025(4)	0.028(5)
C4	0.042(4)	0.047(5)	0.112(7)	0.005(5)	-0.001(4)	0.021(4)
C5	0.078(6)	0.044(5)	0.106(7)	-0.015(5)	-0.003(5)	0.022(5)
C6	0.072(5)	0.049(5)	0.071(5)	-0.008(4)	0.006(4)	0.025(4)
C7	0.069(6)	0.066(6)	0.208(12)	0.042(7)	0.037(6)	0.031(5)
C8	0.038(4)	0.035(4)	0.054(4)	0.007(3)	0.013(3)	0.006(3)
C9	0.047(4)	0.046(4)	0.066(5)	-0.007(3)	0.000(3)	0.010(3)
C10	0.046(4)	0.048(4)	0.049(4)	0.000(3)	0.007(3)	0.016(3)
C11	0.043(3)	0.042(4)	0.044(4)	0.001(3)	0.004(3)	0.010(3)
C12	0.054(4)	0.060(4)	0.041(4)	0.002(3)	0.001(3)	0.010(3)
C13	0.061(4)	0.062(5)	0.054(4)	0.010(4)	0.015(3)	0.017(4)
C14	0.047(4)	0.049(4)	0.042(4)	-0.001(3)	0.005(3)	0.008(3)
C15	0.071(5)	0.050(5)	0.065(5)	0.008(4)	0.010(4)	0.014(4)
C16	0.100(7)	0.056(5)	0.085(6)	0.012(4)	0.012(5)	0.028(5)
C17	0.101(7)	0.043(5)	0.072(5)	-0.007(4)	0.025(5)	-0.001(5)
C18	0.081(5)	0.065(6)	0.088(6)	0.016(5)	-0.006(5)	0.001(5)
C19	0.062(5)	0.063(5)	0.081(5)	0.012(4)	-0.003(4)	0.003(4)
C20	0.110(6)	0.093(6)	0.050(5)	-0.009(4)	0.004(4)	0.031(5)
C21	0.061(4)	0.066(5)	0.062(5)	0.012(4)	-0.007(4)	0.008(4)
C22	0.110(7)	0.136(8)	0.087(6)	0.025(6)	0.012(5)	0.075(6)
C23	0.127(8)	0.114(8)	0.109(8)	0.005(6)	-0.045(6)	0.042(6)
C24	0.034(4)	0.038(4)	0.052(5)	-0.004(3)	0.000(3)	0.011(3)
C25	0.077(5)	0.050(5)	0.059(5)	-0.002(4)	0.002(4)	0.024(4)
C26	0.071(5)	0.043(5)	0.096(7)	-0.009(4)	-0.013(4)	0.018(4)
C27	0.045(4)	0.041(5)	0.100(6)	0.015(4)	0.014(4)	0.021(4)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C28	0.064(5)	0.057(5)	0.072(5)	0.008(4)	0.013(4)	0.027(4)
C29	0.046(4)	0.053(5)	0.065(5)	-0.010(4)	-0.001(3)	0.014(4)
C30	0.077(6)	0.057(6)	0.153(9)	0.036(5)	0.027(6)	0.023(5)
C31	0.045(4)	0.041(4)	0.053(4)	0.007(3)	0.008(3)	0.012(3)
C32	0.067(5)	0.059(5)	0.072(5)	-0.005(4)	0.000(4)	0.032(4)
C33	0.048(4)	0.057(4)	0.053(4)	0.000(3)	0.005(3)	0.022(3)
C34	0.057(4)	0.047(4)	0.048(4)	0.003(3)	0.003(3)	0.017(3)
C35	0.079(5)	0.062(5)	0.049(4)	0.005(3)	0.007(4)	0.029(4)
C36	0.080(5)	0.060(5)	0.067(5)	0.010(4)	0.003(4)	0.035(4)
C37	0.077(5)	0.051(5)	0.038(4)	-0.003(3)	-0.001(4)	-0.003(4)
C38	0.120(7)	0.056(5)	0.079(6)	0.003(4)	-0.015(5)	0.022(5)
C39	0.197(13)	0.064(7)	0.091(8)	-0.001(6)	-0.032(8)	0.029(8)
C40	0.232(17)	0.075(9)	0.068(8)	0.016(7)	-0.011(9)	-0.029(11)
C41	0.178(13)	0.101(9)	0.100(9)	-0.012(7)	0.061(8)	-0.050(9)
C42	0.114(8)	0.081(7)	0.091(7)	-0.012(5)	0.031(6)	-0.008(6)
C43	0.092(6)	0.109(7)	0.071(6)	-0.006(5)	-0.023(5)	0.030(5)
C44	0.131(8)	0.076(5)	0.061(6)	0.009(4)	0.016(5)	0.049(6)
C45	0.133(10)	0.151(10)	0.149(10)	0.034(8)	0.075(8)	0.061(8)
C46	0.215(14)	0.215(14)	0.084(8)	-0.024(9)	0.011(8)	0.129(12)
N1	0.040(3)	0.033(3)	0.055(4)	-0.002(3)	0.002(3)	0.008(3)
N2	0.046(3)	0.046(3)	0.048(3)	0.002(3)	0.009(3)	0.012(3)
N3	0.048(3)	0.036(3)	0.068(4)	-0.002(3)	-0.002(3)	0.013(3)
N4	0.042(3)	0.040(3)	0.045(3)	-0.003(3)	0.001(3)	0.005(3)
O1	0.047(3)	0.103(4)	0.065(3)	0.000(3)	0.020(2)	0.024(3)
O2	0.041(3)	0.065(3)	0.065(3)	-0.008(3)	-0.001(2)	0.008(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O3	0.040(3)	0.056(3)	0.084(4)	-0.012(3)	-0.010(3)	0.009(2)
O4	0.050(3)	0.081(4)	0.087(4)	0.003(3)	0.026(3)	0.022(3)
S1	0.0342(9)	0.0539(11)	0.0555(11)	-0.0021(9)	0.0064(8)	0.0101(8)
S2	0.0360(9)	0.0508(11)	0.0700(13)	0.0004(9)	0.0079(9)	0.0115(9)

Table S12. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å²)

	x/a	y/b	z/c	U(eq)
H2	0.4693	0.2363	0.5258	0.075
H3	0.2670	0.0050	0.5566	0.088
H5	0.2380	-0.1435	0.3245	0.093
H6	0.4370	0.0845	0.2914	0.077
H7A	0.0497	-0.2339	0.5186	0.167
H7B	0.1600	-0.3110	0.4735	0.167
H7C	-0.0069	-0.2829	0.4231	0.167
H9A	0.1343	0.4852	0.3369	0.084
H9B	0.0705	0.5336	0.2498	0.084
H9C	0.2802	0.6110	0.2904	0.084
H10	0.1677	0.2634	0.1390	0.058
H11	-0.1585	0.2887	0.1918	0.054
H13A	0.1515	0.4339	0.0450	0.072
H13B	0.0602	0.5082	0.1065	0.072
H15	0.0452	0.0561	0.2274	0.078
H16	-0.0878	-0.1916	0.2533	0.097

	x/a	y/b	z/c	U(eq)
H17	-0.4053	-0.3255	0.2140	0.095
H18	-0.5874	-0.2057	0.1529	0.105
H19	-0.4537	0.0393	0.1277	0.091
H20A	-0.2237	0.0894	-0.0072	0.131
H20B	-0.0051	0.1544	0.0178	0.131
H20C	-0.0934	0.2232	-0.0546	0.131
H22A	-0.4288	0.4574	0.0745	0.154
H22B	-0.2164	0.5191	0.1121	0.154
H22C	-0.3634	0.3813	0.1504	0.154
H23A	-0.5056	0.3131	-0.0449	0.147
H23B	-0.3858	0.2198	-0.0698	0.147
H25	0.7503	0.9204	0.6607	0.075
H26	0.9471	1.1460	0.6160	0.088
H28	0.7870	0.9928	0.3782	0.075
H29	0.5951	0.7650	0.4230	0.068
H30A	0.9824	1.3182	0.4851	0.143
H30B	1.0036	1.2395	0.4038	0.143
H30C	1.1434	1.2589	0.4854	0.143
H32A	0.9185	0.3869	0.6933	0.097
H32B	1.0599	0.4903	0.6353	0.097
H32C	0.8431	0.4260	0.6058	0.097
H33	1.1954	0.6932	0.7502	0.062
H34	0.9362	0.8089	0.7990	0.062
H36A	0.9112	0.5449	0.8574	0.081
H36B	1.1220	0.5529	0.8669	0.081
H38	1.0260	1.0676	0.8266	0.109

	x/a	y/b	z/c	U(eq)
H39	1.2144	1.3098	0.7987	0.154
H40	1.4688	1.3507	0.7309	0.185
H41	1.5555	1.1675	0.6947	0.186
H42	1.3856	0.9247	0.7312	0.13
H43A	1.3714	0.9230	0.9341	0.144
H43B	1.3820	0.7979	0.8761	0.144
H43C	1.3439	0.7676	0.9697	0.144
H45A	0.7381	0.7412	0.9903	0.206
H45B	0.7431	0.6272	0.9227	0.206
H45C	0.7603	0.7864	0.8972	0.206
H46A	1.2196	0.8991	1.0434	0.19
H46B	1.0178	0.8733	1.0727	0.19
H1N	0.4613	0.5161	0.3655	0.053
H3N	0.6418	0.4791	0.5867	0.063

Table S13. Hydrogen bond distances (Å) and angles (°)

	Donor-H	Acceptor-H	Donor-Acceptor	Angle
C32-H32C···O2	0.96	2.60	3.465(9)	150.6
C33-H33···O4	0.98	2.64	3.539(8)	153.3
N1-H1N···O3	0.86	2.47	3.102(7)	131.4
N3-H3N···O2	0.86	2.31	2.879(7)	123.5

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