# Supporting Information

## Stereodivergent (3+2)-Cycloaddition of Donor-Acceptor Cyclopropanes and Citral Imines Catalyzed by $Yb(NTf_2)_3$/PyBOX

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## 1. General experimental details

Tetrahydrofuran (THF) and toluene (PhMe) were purified by distillation over Na/benzophenone under an argon atmosphere just prior to use or stored over molecular sieves 4Å. Dichloromethane (DCM), 1,2-dichloroethane (DCE) and chloroform ($CHCl_3$) were refluxed and distilled over $P_2O_5$ and stored over molecular sieves 4Å. Dimethylsulfoxide (DMSO), triethylamine ($Et_3N$), pyridine (Py), benzylamine ($BnNH_2$) were refluxed and distilled over $CaH_2$ just prior to use. Methanol (MeOH) was refluxed and distilled with Mg turnings and stored over molecular sieves 4Å. Commercially available citral (*E*/Z 1.5:1) was distilled and stored under argon in the dark. All other reagents were used commercial grade chemicals without additional purification.

TLC analysis was performed on Silufol chromatographic plates using UV light and iodine vapor as visualizing agents. For preparative chromatography, silica gel 60 (0.040−0.063 mm) was used.

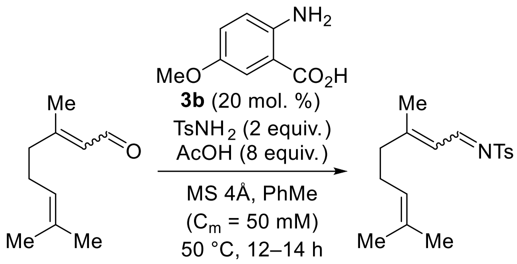
$^1$H and $^{13}$C NMR spectra were recorded on a 300 MHz (300.1 and 75.5 MHz respectively), 400 MHz (400.2 and 100.6 MHz respectively) and 600 MHz (600.1 and 150.9 MHz respectively) spectrometers in $CDCl_3$, containing 0.05% $Me_4Si$ as the internal standard. $^{15}$N NMR spectra were recorded on a 600 MHz spectrometer (60.8 MHz) in $CDCl_3$. Determinations of structures and stereochemistry of obtained compounds and assignments of $^1$H, $^{13}$C and $^{15}$N signals were made with the aid of 1D and 2D gradient/non-gradient COSY, NOESY, HSQC, $^1$H–$^{13}$C and $^1$H–$^{15}$N HMBC spectra. $^{19}$F NMR spectra were recorded on a 300 MHz spectrometer (282.4 MHz); standard—$CFCl_3$. To determine the NMR yields of products, 1,4-dinitrobenzene was used as an internal standard.

High-resolution mass spectra were obtained using simultaneous electrospray ionization (ESI).

The melting points were determined using a Kofler hot-stage microscope.

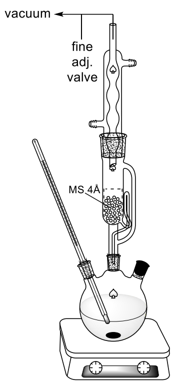
Geranial and neral were synthesized via oxidation of geraniol and nerol by freshly prepared $MnO_2$.[S1] *N*-benzyl-3,7-dimethylocta-2,6-dien-1-imine (**2b**) was prepared using the described synthetic protocol.[S2] *O*-benzylhydroxylamine was synthesized as the free amine using the described synthetic protocol.[S3] $Yb(NTf_2)_3$ was synthesized through a standard synthetic procedure.[S4] Starting donor–acceptor cyclopropanes **5a–m** were synthesized from the corresponding aromatic aldehydes through a standard synthetic sequence of Knoevenagel/Corey-Chaykovsky reactions.[S5]

## 2. General synthetic procedures and spectroscopic data for citral tosylimine 2a



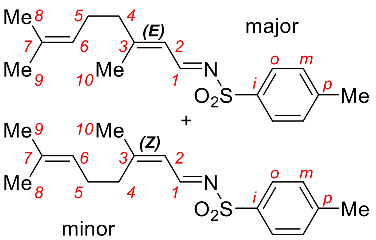

**1** (*E*/*Z* 1.5:1) **2a** (*E*/*Z* 1.5:1)

*Procedure A*: A vial was charged with a magnetic stirring bar, citral (50 mg, 0.329 mmol), $TsNH_2$ (112 mg, 0.658 mmol, 2 equiv.), **3b** (11 mg, 0.066 mmol, 20 mol.%), activated molecular sieves 4Å (0.35 g), 7 mL of dry PhMe and AcOH (150 μL, 2.632 mmol, 8 equiv.). The reaction mixture was stirred for 12 h at 45–50 °C, then cooled, filtrated and evaporated under reduced pressure. The residue was purified by column chromatography (vacuum-dried $SiO_2$; petroleum ether/EtOAc 20:1→15:1→10:1) to afford title compound **2a**. *(Attention: citral tosylimine **2a** is a hygroscopic substance, recommended to be stored in a tightly sealed container under argon, can be stored for at least months in a glovebox.)*




*Gram-scale synthetic procedure B*: In a 500 mL three-necked flask, equipped with a magnetic stirring bar, thermometer, rubber septa and Soxhlet apparatus, connected with condenser, vacuum line and fine adjustment valve, citral (2 g, 13.14 mmol), $TsNH_2$ (3.38 g, 19.71 mmol, 1.5 equiv.), **3b** (434 mg, 2.6 mmol, 20 mol.%), 350 mL of dry PhMe and glacial AcOH (6 mL, 105 mmol, 8 equiv.) were loaded. Activated molecular sieves 4Å (16 g) were loaded into a paper thimble placed in the Soxhlet apparatus. The pressure in the apparatus was adjusted to 120 Torr, then the reaction mixture was stirred and refluxed for 12 h at 45–50 °C. After full consumption of citral (TLC control), the apparatus was filled with argon, the reaction mixture was cooled, filtrated and evaporated under reduced pressure. The residue was purified by column chromatography (vacuum-dried $SiO_2$; petroleum ether/EtOAc 20:1→15:1→10:1) to afford title compound **2a**.

### *N*-((1*E*)-3,7-dimethylocta-2,6-dien-1-ylidene)-4-methylbenzenesulfonamide (2a)

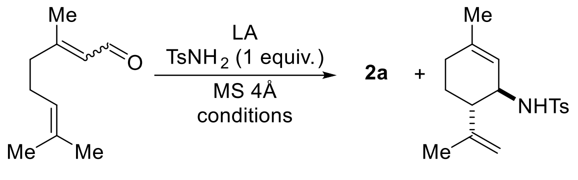



The title compound was obtained by procedures *A* or *B* as a mixture of diastereomers (*E*/*Z* 1.5:1) in summary yield 51 mg (51%) for *A* and 1.2 g (30%) for *B*, yellowish thick oil, $R_f$ = 0.58 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m*/*z*: calcd for $C_{17}H_{23}NNaO_2S^+$ $[M+Na]^+$ 328.1342, found: 328.1333. 2*E*-**2a**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 8.99 (d, $^3J_{1,2}$ = 10.1 Hz, 1H, H(1)), 7.83 (d, $J$ = 8.2 Hz, 2H, 2×H(*o*)), 7.32 (d, $J$ = 8.2 Hz, 2H, 2×H(*m*)), 6.19 (dq, $^3J_{1,2}$ = 10.1, $^4J_{2,10}$ = 1.2 Hz, 1H, H(2)), 5.11–4.98 (m, 1H, H(6)), 2.42 (s, 3H, C(*p'*)–Me), 2.33–2.14 (m, 4H, $CH_2$(4), $CH_2$(5)), 2.12 (d, $^4J_{2,10}$ = 1.2 Hz, 3H, $CH_3$(10)), 1.67 (br.s, 3H, $CH_3$(9)), 1.59 (br.s, 3H, $CH_3$(8)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 167.5 (C(3)), 167.0 (C(1)), 144.2 (C(*p*)), 135.7 (C(*i*)), 133.0 (C(7)), 129.6 (2×CH(*m*)), 127.8 (2×CH(*o*)), 123.2 (CH(2)), 122.3 (CH(6)), 41.0 ($CH_2$(4)), 25.8 ($CH_2$(5)), 25.6 ($CH_3$(9)), 21.5 (C(*p*)–Me), 18.5 ($CH_3$(10)), 17.7 ($CH_3$(8)) ppm. 2*Z*-**2a**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 8.89 (d, $^3J_{1,2}$ = 10.1 Hz, 1H, H(1)), 7.81 (d, $J$ = 8.3 Hz, 2H, 2×H(*o*)), 7.31 (d, $J$ = 8.3 Hz, 2H, 2×H(*m*)), 6.21–6.13 (m, 1H, H(2)), 5.11–4.98 (m, 1H, H(6)), 2.50 (t, $^3J_{4,5}$ = 7.3 Hz, 2H, $CH_2$(4)), 2.42 (s, 3H, C(*p'*)–Me), 2.33–2.14 (m, 2H, $CH_2$(5)), 2.03 (d, $^4J_{2,10}$ = 1.2 Hz, 3H, $CH_3$(10)), 1.67 (br.s, 3H, $CH_3$(9)), 1.59 (br.s, 3H, $CH_3$(8)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 167.1 (C(3)), 166.8 (C(1)), 144.1 (C(*p*)), 135.7 (C(*i*)), 134.1 (C(7)), 129.6 (2×CH(*m*)), 127.7 (2×CH(*o*)), 124.3 (CH(2)), 121.9 (CH(6)), 33.4 ($CH_2$(4)), 26.8 ($CH_2$(5)), 25.6 ($CH_3$(9)), 25.5 ($CH_3$(10)), 21.5 (C(*p*)–Me), 17.8 ($CH_3$(8)) ppm.

**Other reagents tested in the optimization of the synthesis of citral tosylimine 2a:**

- $Si(OEt)_4$ (1 equiv.): <10% **2a**, impurities
- $Yb(OTf)_3$, $Sc(OTf)_3$, $Mg(OTf)_2$, $Zn(OTf)_2$ (10–20 mol. %): up to 30% **2a**, but long process time (approx. weeks) and side ene reaction occurred (chromatographically almost inseparable product **8**), see Table S1
- Inappropriate Lewis acids tested (5–130 mol. %): $BF_3{\cdot}Et_2O$, $TiCl_4$, $GaCl_3$, $Sn(OTf)_2$, $Cu(OTf)_2$, $In(OTf)_3$, $Al(OTf)_3$, $Ga(OTf)_3$ (dirty reaction mixtures in wide variety of conditions)
- Amines tested (20–200 mol. %): $Et_3N$ (quite rapid conversion, but during the reaction a significant amount of by-products are formed), pyridine (almost no reaction)
- Inappropriate solvents: MeCN, THF, EtOAc, EtOH

**Table S1.** The preparation of citral tosylimine **2a** under Lewis acid catalysis.

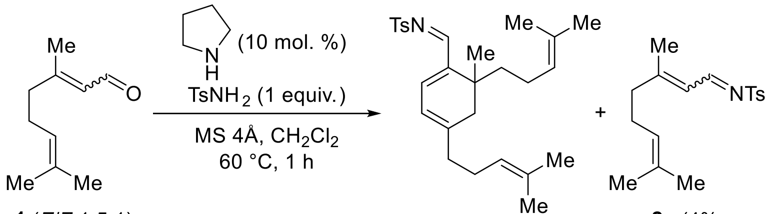



**1** (*E/Z* 1.5:1) **8**

| Entry | LA | Conditions | Conversion[a] **1**, % | Yield[a] **16a** (*E/Z*), % | Yield[a] **18**, % |
|---|---|---|---|---|---|
| 1 | $Yb(OTf)_3$ (10 mol. %) | DCE[b], 40 °C, 12 h, then 80 °C, 36 h | 100 | 22 (2.8:1) | 6 |
| 2 | $Sc(OTf)_3$ (10 mol. %) | DCE, 20 °C, 7 d | 100 | 18 (3:1) | 11 |
| 3 | $Mg(OTf)_2$ (10 mol. %) | DCM[c], 20 °C, 24 h; then 50 °C, 17 h | 76 | 25 (2:1) | – |
| 4 | $Zn(OTf)_2$ (10 mol. %) | DCE, 20 °C, 2 d; then 80 °C, 20 h | 76 | 22 (4.5:1) | 6 |
| 5 | $BF_3{\cdot}Et_2O$ (20 mol. %) | DCM, 20 °C, 24 h | 100 | – | 21 |

[a]Yields and dr were determined from $^1$H NMR spectra. [b]DCE – 1,2-dichloroethane. [c]DCM – dichloromethane.

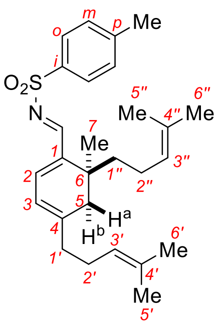
**3. General synthetic procedures and spectroscopic data for cyclohexadiene S1**




**1** (*E/Z* 1.5:1) **S1** (12%) **2a** (4%, *E/Z* 1.5:1)

The mixture of citral (100 mg, 0.657 mmol), $TsNH_2$ (112 mg, 0.657 mmol, 1 equiv.) and pyrrolidine (5.4 μL, 0.066 mmol, 10 mol. %) in $CH_2Cl_2$ (2 mL) was stirred in a sealed vial at 60 °C for 1 h after full consumption of citral (TLC control). Then, the reaction was filtered through a short pad of silica gel, the solvent was removed under reduced pressure. The residue was purified by column chromatography ($SiO_2$; petroleum ether/ethyl acetate 20:1→10:1) to afford title compounds **S1** and **2a** (8 mg, 4%).

**(*E*)-4-methyl-*N*-((6-methyl-4,6-bis(4-methylpent-3-en-1-yl)cyclohexa-1,3-dien-1-yl)methylene)benzenesulfonamide (S1)**



Orange thick oil (34 mg, 12%). $R_f$ = 0.70 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{27}H_{38}NO_2S^+$ $[M+H]^+$ 440.2618, found: 440.2606. $^1$H NMR (300.1 MHz, $CDCl_3$): δ 8.50 (s, 1H, N=CH), 7.80 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.29 (d, *J* = 8.2 Hz, 2H, 2×H(*m*)), 6.78 (d, $^3J_{2,3}$ = 5.9 Hz, 1H, H(2)), 5.93 (br.d, $^3J_{2,3}$ = 5.9 Hz, 1H, H(3)), 5.10–5.03 (m, 1H, H(3’)), 4.83–4.70 (m, 1H, H(3”)), 2.43 (d, $^2J_{5a,5b}$ = 18.0 Hz, 1H, $H_{syn}$(5a)), 2.42 (s, 3H, C(*p*)–Me), 2.23–2.14 (m, 4H, $CH_2$(1’), $CH_2$(2’)), 2.01 (d, $^2J_{5a,5b}$ = 18.0 Hz, 1H, $H_{anti}$(5b)), 2.01 (ddd, $^2J_{1''a,1''b}$ = 12.1, $^3J$ = 7.7, $^3J$ = 1.3 Hz, 1H, H(1”a)), 1.84–1.76 (m, 1H, H(2”a)), 1.68 (br.s, 3H, $CH_3$(6’)), 1.61 (br.s, 3H, $CH_3$(5’)), 1.57 (br.s, 3H, $CH_3$(6”)), 1.59–1.55 (m, 1H, H(2”b)), 1.42 (br.s, 3H, $CH_3$(5”)), 1.26 (ddd, $^3J$ = 13.2, $^2J_{1''a,1''b}$ = 12.1, $^3J$ = 4.9 Hz, 1H, H(1”b)), 1.17 (s, 3H, $CH_3$(7)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.50 (N=CH), 153.2 (C(4)), 147.2 (CH(2)), 143.6 (C(*p*)), 137.4 (C(1)), 136.7 (C(*i*)), 132.5 (C(4’)), 131.0 (C(4”)), 129.5 (2×CH(*m*)), 127.4 (2×CH(*o*)), 124.4 (CH(3”)), 123.0 (CH(3’)), 118.6 (CH(3)), 42.0 ($CH_2$(5)), 38.3 ($CH_2$(1”)), 37.9 ($CH_2$(1’)), 37.1 (C(6)), 25.6 ($CH_3$(6’)), 25.6 ($CH_2$(2’)), 25.5 (CH(3”)), 25.4 ($CH_3$(7)), 23.9 ($CH_2$(2”)), 21.5 (C(*p*)–Me), 17.7 ($CH_3$(5’)), 17.4 ($CH_3$(5”)) ppm.

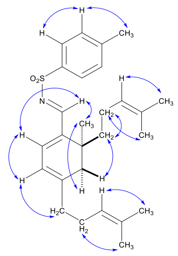
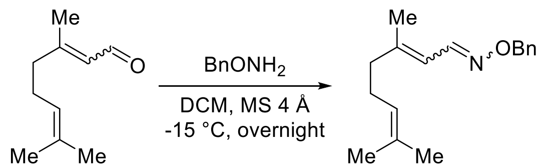


**Figure S1.** Key nOe interactions for **S1** from the NOESY data

## 4. General synthetic procedures and spectroscopic data for citral *O*-benzyl oxime 2c



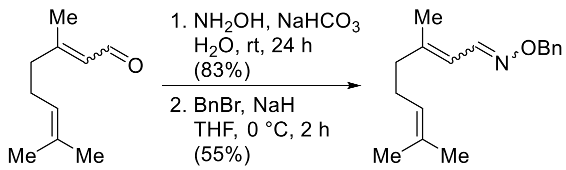

**1**, citral (*E*/*Z* 1.5:1), or *E*-**1**, geranial or *Z*-**1**, neral

**2c** (1*E*/1*Z* 1:1, 2*E*/2*Z* 1.5:1), or 2*E*-**2c** (1*E*/1*Z* 1.2:1) or 2*Z*-**2c** (1*E*/1*Z* 2:1)

Procedure *A*: To a solution of citral, geranial or neral (500 mg, 3.285 mmol, 1.15 equiv.) in 10 mL of $CH_2Cl_2$ were added 3.5 g of activated molecular sieves 4Å and *O*-benzylhydroxylamine (352 mg, 2.857 mmol) in 5 mL of $CH_2Cl_2$, then the mixture was left in a freezer (-15 °C) overnight. Next, the final solution was filtrated and evaporated to obtain almost pure corresponding imine.

*Attempts of chromatographic purification of individual diastereomers of citral O-benzyl oximes on silica gel may result in partial isomerization of the imine at the C(2)=C(3) bond (weakly expressed for the 2E-***2c** *and strongly noticeable for the 2Z-***2c***, up to 25%).*

In case of citral modification, the crude product was purified by column chromatography ($SiO_2$, petroleum ether/EtOAc 15:1) to afford the desired product **2c**.




**1**, citral (*E*/*Z* 1.5:1) 1*E*-**2c** (2*E*/2*Z* 1.2:1)

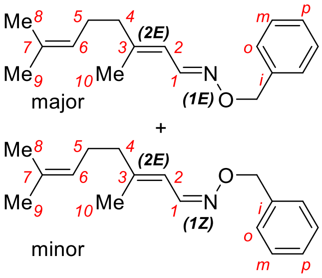
Procedure *B*: To a mixture of citral (*E*/*Z* 1.5/1, 5 g, 32.8 mmol) and $NH_2OH{\cdot}HCl$ (2.852 g, 41.1 mmol, 1.25 equiv.), a solution of $NaHCO_3$ (3.45 g, 41.1 mmol, 1.25 equiv.) in water (36 mL) was added gradually with stirring, and the mixture was stirred for further 24 h. After extraction with diethyl ether (3×100 mL), an organic layer was dried over $Na_2SO_4$ and evaporated to obtain yellowish oil. The product was distilled on a fore vacuum pump (60–68 °C, 0.018–0.020 mbar) to obtain 4.57 g (83%) of citral hydroxylamine as a colorless oil. Characterization data matches those reported in the literature.[S6]

NaH (263 mg, 60% suspension in mineral oil, 1.1 equiv.) was placed in a 50 mL flask with an argon balloon and pre-washed with several portions of dry THF, then 10 mL of dry THF was added. After that, the mixture was cooled to 0 °C, a solution of citral hydroxylamine (1 g, 5.98 mmol) in 10 mL of dry THF was added dropwise followed by addition of a solution of benzyl bromide (1.023 g, 1 equiv.) in dry THF (10 mL). The reaction mixture was stirred for 2 h at room temperature, then quenched with water. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over $Na_2SO_4$, filtered and concentrated in vacuo. The crude product was purified by column chromatography ($SiO_2$, petroleum ether/EtOAc 15:1) to afford the desired product 1*E*-**2c**.

**3,7-dimethylocta-2,6-dienal *O*-benzyl oxime (2c)**

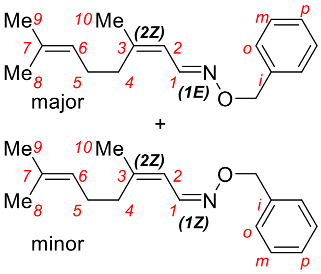
Obtained by procedure *A* from citral as a mixture of diastereomers (1*E*/1*Z* 1:1, 2*E*/2*Z* 1.5:1), colorless oil (638 mg, 85%). $R_f$ = 0.54, 0.66 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{17}H_{24}NO^+$ $[M+H]^+$ 258.1852, found: 258.1844.

**(2*E*)-3,7-dimethylocta-2,6-dienal *O*-benzyl oxime (**2*E*-**2c)**



Obtained by procedure *A* from geranial as a mixture of diastereomers (1*E*/1*Z* 1.2:1), colorless oil (708 mg, 94%). $R_f$ = 0.54 (petroleum ether/EtOAc 3:1). 1*E*,2*E*-**2c**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 8.09 (d, $^3J_{1,2}$ = 10.5 Hz, 1H, H(1)), 7.42–7.23 (m, 5H, 2×H(*o*), 2×H(*m*), H(*p*)), 5.93 (dq, $^3J_{1,2}$ = 10.5, $^4J_{2,10}$ = 1.2 Hz, 1H, H(2)), 5.11–5.02 (m, 1H, H(6)), 5.09 (s, 2H, $CH_2$, Bn), 2.20–2.05 (m, 4H, $CH_2$(4), $CH_2$(5)), 1.79 (d, $^4J_{2,9}$ = 1.2 Hz, 3H, $CH_3$(10)), 1.67 (br.s, 3H, $CH_3$(9)), 1.59 (br.s, 3H, $CH_3$(8)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 148.1 (CH(1)), 147.5 (C(3)), 137.5 (C(*i*)), 132.1 (C(7)), 128.3 (2×CH(*o*)), 128.2 (2×CH(*m*)), 127.8 (CH(*p*)), 123.3 (CH(6)), 117.9 (CH(2)), 75.9 ($CH_2$, Bn), 40.0 ($CH_2$(4)), 26.1 ($CH_2$(5)), 25.6 ($CH_3$(9)), 17.6 ($CH_3$(8)), 17.1 ($CH_3$(10)) ppm. 1*Z*,2*E*-**2c**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.42–7.23 (m, 5H, 2×H(*o*), 2×H(*m*), H(*p*)), 7.30 (d, $^3J_{1,2}$ = 9.9 Hz, 1H, H(1)), 6.49 (dq, $^3J_{1,2}$ = 9.9, $^4J_{2,10}$ = 1.3 Hz, 1H, H(2)), 5.11–5.02 (m, 1H, H(6)), 5.13 (s, 2H, $CH_2$, Bn), 2.20–2.05 (m, 4H, $CH_2$(4), $CH_2$(5)), 1.84 (d, $^4J_{2,9}$ = 1.3 Hz, 3H, $CH_3$(10)), 1.67 (br.s, 3H, $CH_3$(9)), 1.59 (br.s, 3H, $CH_3$(8)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 149.6 (C(3)), 145.2 (CH(1)), 138.1 (C(*i*)), 132.1 (C(7)), 128.3 (2×CH(*o*)), 127.8 (2×CH(*m*)), 127.6 (CH(*p*)), 123.3 (CH(6)), 113.6 (CH(2)), 75.8 ($CH_2$, Bn), 40.2 ($CH_2$(4)), 26.2 ($CH_2$(5)), 25.6 ($CH_3$(9)), 17.6 ($CH_3$(8)), 17.0 ($CH_3$(10)) ppm.

**(2*Z*)-3,7-dimethylocta-2,6-dienal *O*-benzyl oxime** (2*Z*-**2c**)

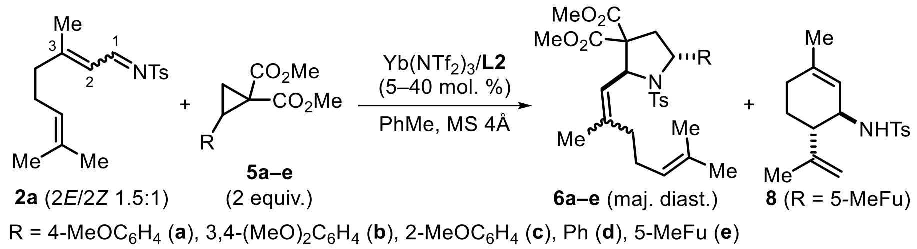


Obtained by procedure *A* from geranial as a mixture of diastereomers (1*E*/1*Z* 2:1), colorless oil (730 mg, 97%). $R_f$ = 0.66 (petroleum ether/EtOAc 3:1). 1*E*,2*Z*-**2c**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 8.06 (d, $^3J_{1,2}$ = 10.4 Hz, 1H, H(1)), 7.39–7.24 (m, 5H, 2×H(*o*), 2×H(*m*), H(*p*)), 5.91 (br.d, $^3J_{1,2}$ = 10.4 Hz, 1H, H(2)), 5.12–5.02 (m, 1H, H(6)), 5.08 (s, 2H, $CH_2$, Bn), 2.28–2.03 (m, 4H, $CH_2$(4), $CH_2$(5)), 1.84 (d, $^4J_{2,9}$ = 1.1 Hz, 3H, $CH_3$(10)), 1.66 (br.s, 3H, $CH_3$(9)), 1.58 (br.s, 3H, $CH_3$(8)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 147.9 (CH(1)), 147.6 (C(3)), 137.6 (C(*i*)), 132.5 (C(7)), 128.3 (2×CH(*o*)), 128.2 (2×CH(*m*)), 127.8 (CH(*p*)), 123.1 (CH(6)), 118.8 (CH(2)), 75.8 ($CH_2$, Bn), 32.7 ($CH_2$(4)), 26.7 ($CH_2$(5)), 25.6 ($CH_3$(9)), 24.2 ($CH_3$(10)), 17.6 ($CH_3$(8)) ppm. 1*Z*,2*Z*-**2c**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.39–7.24 (m, 5H, 2×H(*o*), 2×H(*m*), H(*p*)), 7.28 (d, $^3J_{1,2}$ = 9.9 Hz, 1H, H(1)), 6.49 (br.d, $^3J_{1,2}$ = 9.9 Hz, 1H, H(2)), 5.12 (s, 2H, $CH_2$, Bn), 5.12–5.02 (m, 1H, H(6)), 2.28–2.03 (m, 4H, $CH_2$(4), $CH_2$(5)), 1.86 (d, $^4J_{2,9}$ = 1.1 Hz, 3H, $CH_3$(10)), 1.66 (br.s, 3H, $CH_3$(9)), 1.58 (br.s, 3H, $CH_3$(8)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 149.9 (C(3)), 144.9 (CH(1)), 138.1 (C(*i*)), 132.6 (C(7)), 128.3 (2×CH(*o*)), 127.9 (2×CH(*m*)), 127.6 (CH(*p*)), 123.0 (CH(6)), 114.4 (CH(2)), 75.9 ($CH_2$, Bn), 32.6 ($CH_2$(4)), 26.8 ($CH_2$(5)), 25.6 ($CH_3$(9)), 24.3 ($CH_3$(10)), 17.6 ($CH_3$(8)) ppm.

**3,7-dimethylocta-2,6-dienal *O*-benzyl oxime** (1*E*-**2c**)

Obtained by procedure *B* from citral as a mixture of diastereomers (1*E*/1*Z* 20:1, 2*E*/2*Z* 1.2:1), yellowish oil (840 mg, 55%). $R_f$ = 0.54, 0.66 (petroleum ether/EtOAc 3:1).

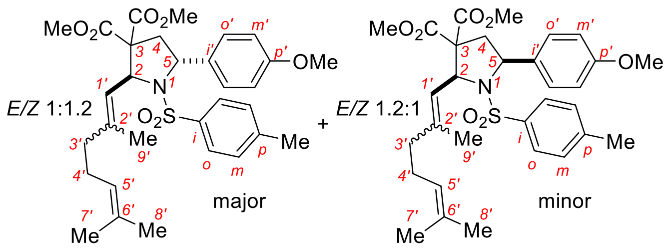
## 5. General synthetic procedures and spectroscopic data for *N*-tosylpyrrolidines 6 and cyclohexene 8



Procedure *A*: All operations were performed under dry argon atmosphere. A flame-dried vial was charged with a magnetic stirring bar, ligand **L2** (0.9–5.9 mg, 0.004–0.030 mmol, 6–42 mol. %), $Yb(NTf_2)_3$ (3.3–26.7 mg, 0.003–0.026 mmol, 5–40 mol. %), activated MS 4Å and 2 mL of dry PhMe, followed by the ultrasonic irradiation for 1 h. After the preparation of catalytic complex, the DAC **5a–e** (0.131–0.262 mmol, 2–4 equiv.) and citral tosylimine **2a** (20 mg, 0.066 mmol) were dissolved in 1 ml of PhMe and added to the catalyst at once. Then, the reaction mixture was stirred under conditions specified. After that, the reaction mixture was passed through a short pad of silica gel, the solvent was removed under reduced pressure. The residue was purified by column chromatography ($SiO_2$; petroleum ether/ethyl acetate) to afford title compounds **6**.

Procedure *B, slow addition*: All operations were performed under dry argon atmosphere. A flame-dried flask equipped with a rubber septa and magnetic stirring bar, was charged with ligand **L2** (1.8 mg, 0.008 mmol, 12 mol. %), $Yb(NTf_2)_3$ (6.6 mg, 0.006 mmol, 10 mol. %), activated MS 4Å and 2 mL of dry PhMe, followed by the ultrasonic irradiation for 1 h. After the preparation of catalytic complex, the solution of citral tosylimine **2a** (20 mg, 0.066 mmol) in 1 ml of PhMe was added to the catalyst solution. Then, the solution of **5e** (16 mg, 0.066 mmol, 1 equiv.) in 2 ml of PhMe was slowly added to the mixture using a syringe pump over 3 hours (0.7 ml/h) followed by stirring overnight. Next day the second portion of **5e** (16 mg, 0.066 mmol, 1 equiv.) in 2 ml of PhMe was slowly added to the mixture using a syringe pump over 10 hours (0.2 ml/h). After that, the reaction mixture was passed through a short pad of silica gel, the solvent was removed under reduced pressure. The residue was purified by column chromatography ($SiO_2$; petroleum ether/ethyl acetate 15:1→12:1→10:1) to afford title compounds **6e** and **8**.

**Dimethyl 2-(2,6-dimethylhepta-1,5-dien-1-yl)-5-(4-methoxyphenyl)-1-tosylpyrrolidine-3,3-dicarboxylate (6a)**



The title compound was prepared according to the procedure *A* from **2a**, **5a** (35 mg, 0.131 mmol), $Yb(NTf_2)_3$ (3.3 mg, 0.003 mmol, 5 mol.%), **L2** (0.9 mg, 0.004 mmol, 6 mol.%) at 20 °C, 48 h as a mixture of diastereomers, *trans* (*E*/*Z* 1:1.2)/*cis* (*E*/*Z* 1.2:1) 2.7:1, in 36 mg yield (97%). Eluent: petroleum ether/EtOAc 5:1. Yellowish thick oil, $R_f$ = 0.29 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{31}H_{40}NO_7S^+$ $[M+H]^+$ 570.2520, found: 570.2513. NMR spectra were recorded at 300 and 600 MHz. *E,trans*-**6a**: $^1H$ NMR (600.1 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.12 (d, *J* = 8.2 Hz, 2H, 2×H(*m*)), 7.04 (d, *J* = 8.9 Hz, 2H, 2×H(*o'*)), 6.70 (d, *J* = 8.9 Hz, 2H, 2×H(*m'*)), 5.75 (d, $^3J_{2,1'}$ = 10.9 Hz, 1H, H(2)), 5.13–5.00 (m, 1H, H(5')), 4.90 (dd, $^3J_{4a,5}$ = 9.7, $^3J_{4b,5}$ = 2.4 Hz, 1H, H(5)), 4.80 (dq, $^3J_{2,1'}$ = 10.9, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 3.75 (s, 3H, OMe), 3.57 and 3.53 (both s, 2×3H, 2 $CO_2Me$), 3.22 (dd, $^2J_{4a,4b}$ = 13.9, $^3J_{4a,5}$ = 9.7 Hz, 1H, $H_{syn}$(4a)), 2.44 (dd, $^2J_{4a,4b}$ = 13.9, $^3J_{4b,5}$ = 2.4 Hz, 1H, $H_{anti}$(4b)), 2.36 (s, 3H, C(*p*)–Me), 2.16–1.98 (m, 2H, $CH_2$(4')), 1.96–1.81 (m, 2H, $CH_2$(3')), 1.84 (d, $^4J_{1',9'}$ = 1.3 Hz, 1H, $CH_3$(9')), 1.69 (br.s, 3H, $CH_3$(8')), 1.59 (br.s, 3H, $CH_3$(7')) ppm. $^{13}C$ NMR (150.9 MHz, $CDCl_3$): δ 169.9 and 167.3 (2 COO), 158.6 (C(*p'*)), 142.7 (C(*p*)), 142.5 (C(2')), 138.1 (C(*i*)), 133.1 (C(*i'*)), 131.8 (C(6')), 128.7 (2×CH(*m*)), 128.0 (2×CH(*o'*)), 127.8 (2×CH(*o*)), 123.6 (CH(5')), 118.3 (CH(1')), 113.3 (2×CH(*m'*)), 62.8 (CH(2)), 62.8 (C(3)), 60.6 (CH(5)), 55.2 (OMe), 52.9 and 52.6 (2 $CO_2Me$), 40.4 ($CH_2$(4)), 39.7 ($CH_2$(3')), 26.2 ($CH_2$(4')), 25.5 ($CH_3$(8')), 21.4 (C(*p*)–Me), 17.7 ($CH_3$(7')), 16.4 ($CH_3$(9')) ppm. $^{15}N$ NMR (60.8 MHz, $CDCl_3$; reconstructed from $^1H$–$^{15}N$ HMBC): δ -266.8 (s) ppm. *Z,trans*-**6a**: $^1H$ NMR (600.1 MHz, $CDCl_3$): δ 7.48

(d, $J$ = 8.2 Hz, 2H, 2×H(*o*)), 7.14 (d, $J$ = 8.2 Hz, 2H, 2×H(*m*)), 7.09 (d, $J$ = 9.0 Hz, 2H, 2×H(*o'*)), 6.73 (d, $J$ = 9.0 Hz, 2H, 2×H(*m'*)), 5.78 (d, $^{3}J_{2,1'}$ = 11.4 Hz, 1H, H(2)), 5.30–5.21 (m, 1H, H(5')), 4.93 (dd, $^{3}J_{4a,5}$ = 9.5, $^{3}J_{4b,5}$ = 2.4 Hz, 1H, H(5)), 4.65 (dq, $^{3}J_{2,1'}$ = 11.0, $^{4}J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 3.75 (s, 3H, OMe), 3.55 and 3.48 (both s, 2×3H, 2 $CO_2Me$), 3.16 (dd, $^{2}J_{4a,4b}$ = 13.8, $^{3}J_{4a,5}$ = 9.5 Hz, 1H, $H_{syn}$(4a)), 2.46 (dd, $^{2}J_{4a,4b}$ = 13.8, $^{3}J_{4b,5}$ = 2.4 Hz, 1H, $H_{anti}$(4b)), 2.37 (s, 3H, C(*p*)–Me), 2.34–2.17 (m, 3H, $CH_2$(3'), H(4'a)), 2.16–1.98 (m, 1H, H(4'b)), 1.73 (br.s, 3H, $CH_3$(8')), 1.70 (br.s, 3H, $CH_3$(7')), 1.60 (d, $^{4}J_{1',9'}$ = 1.3 Hz, 1H, $CH_3$(9')) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): δ 169.7 and 167.4 (2 COO), 158.6 (C(*p'*)), 142.7 (C(*p*)), 142.6 (C(2')), 138.3 (C(*i*)), 133.2 (C(*i'*)), 131.9 (C(6')), 128.7 (2×CH(*m*)), 127.9 (2×CH(*o'*) and 2×CH(*o*)), 124.2 (CH(5')), 119.1 (CH(1')), 113.3 (2×CH(*m'*)), 63.0 (C(3)), 62.2 (CH(2)), 60.7 (CH(5)), 55.2 (OMe), 52.8 and 52.7 (2 $CO_2Me$), 40.4 ($CH_2$(4)), 32.2 ($CH_2$(3')), 26.2 ($CH_2$(4')), 25.6 ($CH_3$(8')), 23.4 ($CH_3$(9')), 21.4 (C(*p*)–<u>Me</u>), 17.6 ($CH_3$(7')) ppm. $^{15}$N NMR (60.8 MHz, $CDCl_3$; reconstructed from $^{1}$H–$^{15}$N HMBC): δ -266.8 (s) ppm. *E,cis*-**6a**: $^{1}$H NMR (600.1 MHz, $CDCl_3$): δ 7.21 (d, $J$ = 8.2 Hz, 2H, 2×H(*o*)), 7.04 (d, $J$ = 8.6, 2H, 2×H(*o'*)), 6.99 (d, $J$ = 8.2 Hz, 2H, 2×H(*m*)), 6.67 (d, $J$ = 8.6, 2H, 2×H(*m'*)), 5.76 (d, $^{3}J_{2,1'}$ = 10.7 Hz, 1H, H(2)), 5.17 (br.d, $^{3}J_{2,1'}$ = 10.7 Hz, 1H, H(1')), 5.13–5.00 (m, 1H, H(5')), 4.55 (t, $^{3}J_{4,5}$ = 9.0 Hz, 1H, H(5)), 3.78 and 3.61 (both s, 2×3H, 2 $CO_2Me$), 3.76 (s, 3H, OMe), 2.70 (d, $^{3}J_{4,5}$ = 9.0 Hz, 2H, $CH_2$(4)), 2.31 (s, 3H, C(*p*)–Me), 2.16–1.98 (m, 2H, $CH_2$(4')), 1.96–1.81 (m, 2H, $CH_2$(3')), 1.88 (d, $^{4}J_{1',9'}$ = 1.3 Hz, 1H, $CH_3$(9')), 1.70 (br.s, 3H, $CH_3$(8')), 1.63 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): δ 169.7 and 167.3 (2 COO), 159.1 (C(*p'*)), 142.2 (C(*p*)), 141.4 (C(2')), 138.0 (C(*i*)), 131.8 (C(6')), 131.1 (C(*i'*)), 128.6 and 128.5 (2×CH(*m*) and 2×CH(*o'*)), 127.2 (2×CH(*o*)), 123.7 (CH(5')), 121.3 (CH(1')), 113.6 (2×CH(*m'*)), 62.8 (C(3)), 61.9 (CH(2)), 61.0 (CH(5)), 55.2 (OMe), 53.3 and 52.5 (2 $CO_2Me$), 41.7 ($CH_2$(4)), 39.7 ($CH_2$(3')), 26.6 ($CH_2$(4')), 25.6 ($CH_3$(8')), 21.3 (C(*p*)–<u>Me</u>), 17.7 ($CH_3$(7')), 16.5 ($CH_3$(9')) ppm. $^{15}$N NMR (60.8 MHz, $CDCl_3$; reconstructed from $^{1}$H–$^{15}$N HMBC): δ -264.5 (s) ppm. *Z,cis*-**6a**: $^{1}$H NMR (600.1 MHz, $CDCl_3$): δ 7.22 (d, $J$ = 8.2 Hz, 2H, 2×H(*o*)), 7.05 (d, $J$ = 8.7 Hz, 2H, 2×H(*o'*)), 7.01 (d, $J$ = 8.2 Hz, 2H, 2×H(*m*)), 6.68 (d, $J$ = 8.6, 2H, 2×H(*m'*)), 5.77 (d, $^{3}J_{2,1'}$ = 10.7 Hz, 1H, H(2)), 5.30–5.21 (m, 1H, H(5')), 5.17 (br.d, $^{3}J_{2,1'}$ = 10.7 Hz, 1H, H(1')), 4.51 (t, $^{3}J_{4,5}$ = 8.9 Hz, 1H, H(5)), 3.75 and 3.61 (both s, 2×3H, 2 $CO_2Me$), 3.75 (s, 3H, OMe), 2.71 (d, $^{3}J_{4,5}$ = 8.9 Hz, 2H, $CH_2$(4)), 2.32 (s, 3H, C(*p*)–Me), 2.34–2.17 (m, 3H, $CH_2$(3'), H(4'a)), 2.16–1.98 (m, 1H, H(4'b)), 1.78 (d, $^{4}J_{1',9'}$ = 1.3 Hz, 1H, $CH_3$(9')), 1.72 (br.s, 3H, $CH_3$(8')), 1.70 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): δ 169.7 and 167.4 (2 COO), 159.1 (C(*p'*)), 142.2 (C(*p*)), 141.5 (C(2')), 137.8 (C(*i*)), 131.9 (C(6')), 131.1 (C(*i'*)), 128.6 and 128.5 (2×CH(*m*) and 2×CH(*o'*)), 127.3 (2×CH(*o*)), 124.1 (CH(5')), 121.8 (CH(1')), 113.6 (2×CH(*m'*)), 62.9 (C(3)), 61.9 (CH(2)), 60.8 (CH(5)), 55.2 (OMe), 53.3 and 52.6 (2 $CO_2Me$), 41.8 ($CH_2$(4)), 32.3 ($CH_2$(3')), 26.5 ($CH_2$(4')), 25.7 ($CH_3$(8')), 23.5 ($CH_3$(9')), 21.3 (C(*p*)–<u>Me</u>), 17.6 ($CH_3$(7')) ppm. $^{15}$N NMR (60.8 MHz, $CDCl_3$; reconstructed from $^{1}$H–$^{15}$N HMBC): δ -264.5 (s) ppm.

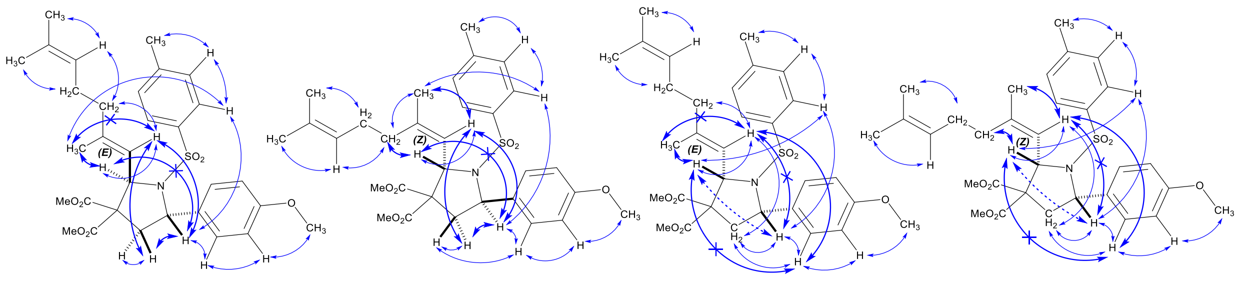
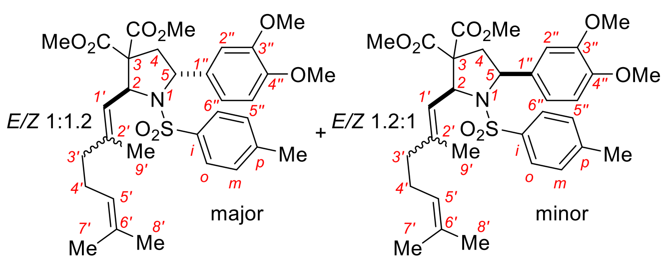


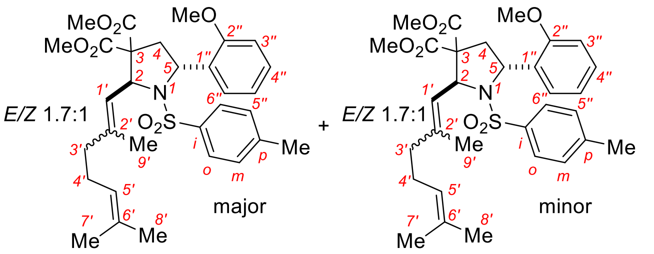
**Figure S2.** Key nOe interactions for the isomers of **6a** from the NOESY data

**Dimethyl 5-(3,4-dimethoxyphenyl)-2-(2,6-dimethylhepta-1,5-dien-1-yl)-1-tosylpyrrolidine-3,3-dicarboxylate (6b)**



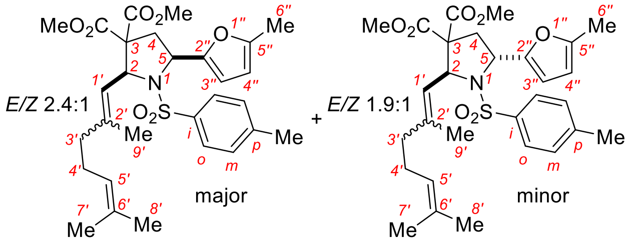

The title compound was prepared according to the procedure *A* from **2a**, **5b** (39 mg, 0.131 mmol), $Yb(NTf_2)_3$ (3.3 mg, 0.003 mmol, 5 mol.%), **L2** (0.9 mg, 0.004 mmol, 6 mol.%) at 20 °C, 48 h as a mixture of diastereomers, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 3.7:1, in 35 mg yield (89%). Eluent: petroleum ether/EtOAc 2:1. Yellowish thick oil, $R_f$ = 0.13 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{32}H_{42}NO_8S^+$ [M+H]$^+$ 600.2626, found: 600.2625. *E,trans*-**6b**: $^1$H NMR (300.1 MHz, CDCl$_3$): δ 7.47 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.12 (d, *J* = 8.2 Hz, 2H, 2×H(*m*)), 6.79–6.66 (m, 2H, H(5''), H(6'')), 6.58 (d, $^4J_{2'',6''}$ = 1.7 Hz, 1H, H(2'')), 5.76 (d, $^3J_{2,1'}$ = 11.0 Hz, 1H, H(2)), 5.14–5.00 (m, 1H, H(5')), 4.94 (dd, $^3J_{4a,5}$ = 9.9, $^3J_{4b,5}$ = 2.6 Hz, 1H, H(5)), 4.89 (dq, $^3J_{2,1'}$ = 11.0, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 3.85 and 3.78 (both s, 2×3H, 2 OMe), 3.60 and 3.56 (both s, 2×3H, 2 $CO_2$Me), 3.29 (dd, $^2J_{4a,4b}$ = 14.0, $^3J_{4a,5}$ = 9.9 Hz, 1H, $H_{syn}$(4a)), 2.43 (dd, $^2J_{4a,4b}$ = 14.0, $^3J_{4b,5}$ = 2.6 Hz, 1H, $H_{anti}$(4b)), 2.38 (s, 3H, C(*p*)–Me), 2.20–2.00 (m, 2H, $CH_2$(4')), 2.00–1.90 (m, 2H, $CH_2$(3')), 1.86 (d, $^4J_{1',9'}$ = 1.3 Hz, 1H, $CH_3$(9')), 1.71 (br.s, 3H, $CH_3$(8')), 1.61 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 170.2 and 167.3 (2 COO), 148.5 (CH(3'')), 148.1 (CH(4'')), 142.7 (C(*p*)), 142.5 (C(2')), 138.2 (C(*i*)), 133.5 (C(1'')), 131.8 (C(6')), 128.7 (2×CH(*m*)), 127.9 (2×CH(*o*)), 123.7 (CH(5')), 119.3 (CH(6'')), 118.3 (CH(1')), 110.5 (CH(5'')), 109.9 (CH(2'')), 62.9 (C(3)), 62.8 (CH(2)), 60.9 (CH(5)), 55.9 and 55.5 (OMe), 52.9 and 52.6 (2 $CO_2$Me), 40.4 ($CH_2$(4)), 39.8 ($CH_2$(3')), 26.2 ($CH_2$(4')), 25.6 ($CH_3$(8')), 21.4 (C(*p*)–<u>Me</u>), 17.7 ($CH_3$(7')), 16.5 ($CH_3$(9')) ppm. *Z,trans*-**6b**: $^1$H NMR (300.1 MHz, CDCl$_3$): δ 7.49 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.15 (d, *J* = 8.2, 2H, 2×H(*m*)), 6.79–6.66 (m, 2H, H(5''), H(6'')), 6.64 (d, $^4J_{2'',6''}$ = 1.7 Hz, 1H, H(2'')), 5.80 (d, $^3J_{2,1'}$ = 11.0 Hz, 1H, H(2)), 5.33–5.21 (m, 1H, H(5')), 4.95 (dd, $^3J_{4a,5}$ = 9.6, $^3J_{4b,5}$ = 2.4 Hz, 1H, H(5)), 4.74 (dq, $^3J_{2,1'}$ = 11.0, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 3.85 and 3.81 (both s, 2×3H, 2 OMe), 3.59 and 3.52 (both s, 2×3H, 2 $CO_2$Me), 3.24 (dd, $^2J_{4a,4b}$ = 13.9, $^3J_{4a,5}$ = 9.6 Hz, 1H, $H_{syn}$(4a)), 2.46 (dd, $^2J_{4a,4b}$ = 13.9, $^3J_{4b,5}$ = 2.4 Hz, 1H, $H_{anti}$(4b)), 2.39 (s, 3H, C(*p*)–Me), 2.35–2.20 (m, 3H, $CH_2$(3'), H(4'a)), 2.20–2.00 (m, 1H, H (4'b)), 1.75 (br.s, 3H, $CH_3$(8')), 1.71 (br.s, 3H, $CH_3$(7')), 1.64 (d, $^4J_{1',9'}$ = 1.3 Hz, 1H, $CH_3$(9')) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 169.9 and 167.4 (2 COO), 148.5 (CH(3'')), 148.0 (CH(4'')), 142.7 (C(*p*)), 142.6 (C(2')), 138.3 (C(*i*)), 133.7 (C(1'')), 132.0 (C(6')), 128.7 (2×CH(*m*)), 127.8 (2×CH(*o*)), 124.2 (CH(5')), 119.2 (CH(6'')), 119.0 (CH(1')), 110.5 (CH(5'')), 109.9 (CH(2'')), 63.0 (C(3)), 62.4 (CH(2)), 60.8 (CH(5)), 55.9 and 55.6 (2 OMe), 52.9 and 52.8 (2 $CO_2$Me), 40.4 ($CH_2$(4)), 32.2 ($CH_2$(3')), 26.2 ($CH_2$(4')), 25.7 ($CH_3$(8')), 23.5 ($CH_3$(9')), 21.4 (C(*p*)–<u>Me</u>), 17.6 ($CH_3$(7')) ppm. *E,cis*-**6b**: $^1$H NMR (300.1 MHz, CDCl$_3$): δ 7.20 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.01 (d, *J* = 8.2, 2H, 2×H(*m*)), 6.79–6.66 (m, 2H, H(5''), H(6'')), 6.52 (d, $^4J_{2'',6''}$ = 1.7 Hz, 1H, H(2'')), 5.84 (d, $^3J_{2,1'}$ = 10.9 Hz, 1H, H(2)), 5.17 (br.d, $^3J_{2,1'}$ = 10.9 Hz, 1H, H(1')), 5.14–5.00 (m, 1H, H(5')), 4.62 (t, $^3J_{4,5}$ = 11.1 Hz, 1H, H(5)), 3.86 and 3.63 (both s, 2×3H, 2 $CO_2$Me), 3.85 and 3.65 (both s, 2×3H, 2 OMe), 2.78–2.68 (m, 2H, $CH_2$(4)), 2.33 (s, 3H, C(*p*)–Me), 2.20–2.00 (m, 2H, $CH_2$(3')), 2.00–1.90 (m, 2H, $CH_2$(4')), 1.93 (d, $^4J_{1',9'}$ = 1.3 Hz, 1H, $CH_3$(9')), 1.72 (br.s, 3H, $CH_3$(8')), 1.65 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 169.8 and 167.4 (2 COO), 148.7 and 148.5 (CH(3'') and CH(4'')), 142.3 (C(*p*)), 141.6 (C(2')), 138.3 (C(*i*)), 131.8 (C(6')), 131.4 (C(1'')), 128.5 (2×CH(*m*)), 127.2 (2×CH(*o*)), 123.5 (CH(5')), 121.1 (CH(1')), 120.1 (CH(6'')), 110.7 (CH(5'')), 110.1 (CH(2'')), 62.9 (C(3)), 62.2 (CH(5)), 61.0 (CH(2)), 55.9 and 55.2 (2 OMe), 53.4 and 52.5 (2 $CO_2$Me), 41.8 ($CH_2$(4)), 39.9 ($CH_2$(3')), 26.6 ($CH_2$(4')), 25.6 ($CH_3$(8')), 21.3 (C(*p*)–<u>Me</u>), 17.7 ($CH_3$(7')), 16.6 ($CH_3$(9')) ppm. *Z,cis*-**6b**: $^1$H NMR (300.1 MHz, CDCl$_3$): δ 7.20 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.01 (d, *J* = 8.2 Hz, 2H, 2×H(*m*)), 6.79–6.66 (m, 2H, H(5''), H(6'')), 6.52 (d, $^4J_{2'',6''}$ = 1.7 Hz, 1H, H(2'')), 5.85 (d, $^3J_{2,1'}$ = 10.9 Hz, 1H, H(2)), 5.33–5.21 (m, 1H, H(5')), 5.17 (br.d, $^3J_{2,1'}$ = 10.9 Hz, 1H, H(1')), 4.60 (t, $^3J_{4,5}$ = 11.2 Hz, 1H, H(5)), 3.86 and 3.65 (both s, 2×3H, 2 $CO_2$Me), 3.82 and 3.65 (both s, 2×3H, 2 OMe), 2.78–2.68 (m, 2H, $CH_2$(4)), 2.34 (s, 3H, C(*p*)–Me), 2.35–2.20 (m, 3H, $CH_2$(3'), H(4'a)), 2.20–2.00 (m, 1H, H (4'b)), 1.80 (d, $^4J_{1',9'}$ = 1.3 Hz, 1H, $CH_3$(9')), 1.75 (br.s, 3H, $CH_3$(8')), 1.72 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 169.8 and 167.4 (2 COO), 148.7 and 148.5 (CH(3'') and CH(4'')), 142.3 (C(*p*)), 141.6 (C(2')), 137.7 (C(*i*)), 132.0 (C(6')), 131.4 (C(1'')), 128.4 (2×CH(*m*)), 127.2 (2×CH(*o*)), 124.1 (CH(5')), 121.1 (CH(1')), 120.2 (CH(6'')), 110.7 (CH(5'')), 110.0 (CH(2'')), 62.9 (C(3)), 62.5 (CH(5)), 60.8 (CH(2)), 55.9 and 55.3 (2 OMe), 53.4 and 52.7 (2 $CO_2$Me), 41.9 ($CH_2$(4)), 32.3 ($CH_2$(3')), 26.6 ($CH_2$(4')), 25.7 ($CH_3$(8')), 23.6 ($CH_3$(9')), 21.3 (C(*p*)–<u>Me</u>), 17.6 ($CH_3$(7')) ppm.

**Dimethyl 2-(2,6-dimethylhepta-1,5-dien-1-yl)-5-(2-methoxyphenyl)-1-tosylpyrrolidine-3,3-dicarboxylate (6c)**



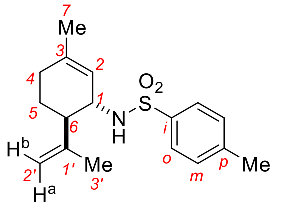

The title compound was prepared according to the procedure *A* from **2a**, **5c** (69 mg, 0.262 mmol, 4 equiv.), $Yb(NTf_2)_3$ (26.7 mg, 0.026 mmol, 40 mol.%), **L2** (5.9 mg, 0.030 mmol, 42 mol.%) at 40 °C, 72 h as a mixture of diastereomers, *trans* (*E/Z* 1.7:1)/*cis* (*E/Z* 1.7:1) 3.5:1, in 20 mg yield (54%). Eluent: petroleum ether/EtOAc 6:1. Yellowish thick oil, $R_f$ = 0.50 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{31}H_{39}KNO_7S^+$ $[M+K]^+$ 608.2079, found: 608.2085. *E,trans*-**6c**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.50–7.37 (m, 1H, H(6”)), 7.21–7.11 (m, 3H, H(4”), 2×H(*m*)), 6.93–6.82 (m, 1H, H(5”)), 6.82–6.72 (m, 1H, H(3”)), 5.77 (d, $^3J_{2,1'}$ = 11.0 Hz, 1H, H(2)), 5.41–5.17 (m, 1H, H(5)), 5.06–4.87 (m, 1H, H(5’)), 4.61 (br.d, $^3J_{2,1'}$ = 11.0 Hz, 1H, H(1’)), 3.81 (s, 3H, OMe), 3.53 and 3.35 (both s, 2×3H, 2 $CO_2Me$), 3.05 (dd, $^2J_{4a,4b}$ = 13.5, $^3J_{4a,5}$ = 9.3 Hz, 1H, $H_{syn}$(4a)), 2.51 (br.d, $^2J_{4a,4b}$ = 13.5, 1H, $H_{anti}$(4b)), 2.38 (s, 3H, C(*p*)–Me), 2.18–1.99 (m, 2H, $CH_2$(4’)), 1.92–1.80 (m, 2H, $CH_2$(3’)), 1.84 (br.s, 1H, $CH_3$(9’)), 1.68 (br.s, 3H, $CH_3$(8’)), 1.57 (br.s, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 169.6 and 167.4 (2 COO), 155.7 (C(2”)), 142.8 (C(*p*)), 142.4 (C(2’)), 138.3 (C(*i*)), 131.8 (C(6’)), 129.6 (C(1”)), 128.9 (2×CH(*m*)), 128.1 (CH(4”) and CH(6”)), 127.9 (2×CH(*o*)), 123.7 (CH(5’)), 118.9 (CH(1’)), 119.7 (CH(5”)), 109.7 (CH(3”)), 63.1 (C(3)), 62.2 (CH(2)), 57.5 (CH(5)), 55.1 (OMe), 52.7 and 52.5 (2 $CO_2Me$), 38.3 ($CH_2$(4)), 39.7 ($CH_2$(3’)), 26.1 ($CH_2$(4’)), 25.6 ($CH_3$(8’)), 21.4 (C(*p*)–Me), 17.7 ($CH_3$(7’)), 16.5 ($CH_3$(9’)) ppm. *Z,trans*-**6c**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.50–7.37 (m, 1H, H(6”)), 7.21–7.11 (m, 3H, H(4”), 2×H(*m*)), 6.93–6.82 (m, 1H, H(5”)), 6.82–6.72 (m, 1H, H(3”)), 5.81 (d, $^3J_{2,1'}$ = 11.0 Hz, 1H, H(2)), 5.41–5.17 (m, 2H, H(5), H(5’)), 4.48 (br.d, $^3J_{2,1'}$ = 11.0 Hz, 1H, H(1’)), 3.82 (s, 3H, OMe), 3.52 and 3.32 (both s, 2×3H, 2 $CO_2Me$), 3.01 (dd, $^2J_{4a,4b}$ = 13.5, $^3J_{4a,5}$ = 9.3 Hz, 1H, $H_{syn}$(4a)), 2.53 (br.d, $^2J_{4a,4b}$ = 13.5, 1H, $H_{anti}$(4b)), 2.40 (s, 3H, C(*p*)–Me), 2.31–2.18 (m, 3H, $CH_2$(3’), H(4’a)), 2.18–1.99 (m, 1H, H(4’b)), 1.74 (br.s, 3H, $CH_3$(8’)), 1.71 (br.s, 3H, $CH_3$(7’)), 1.53 (br.s, 1H, $CH_3$(9’)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 169.4 and 167.5 (2 COO), 155.7 (C(2”)), 142.7 (C(*p*)), 142.5 (C(2’)), 138.6 (C(*i*)), 132.0 (C(6’)), 129.5 (C(1”)), 128.8 (2×CH(*m*)), 128.1 (CH(4”) and CH(6”)), 127.9 (2×CH(*o*)), 124.2 (CH(5’)), 119.8 (CH(1’)), 119.7 (CH(5”)), 109.7 (CH(3”)), 63.3 (C(3)), 61.7 (CH(2)), 57.2 (CH(5)), 55.1 (OMe), 52.7 and 52.7 (2 $CO_2Me$), 38.3 ($CH_2$(4)), 32.2 ($CH_2$(3’)), 26.3 ($CH_2$(4’)), 25.7 ($CH_3$(8’)), 23.5 ($CH_3$(9’)), 21.4 (C(*p*)–Me), 17.6 ($CH_3$(7’)) ppm. *E,cis*-**6c**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.21–7.11 (m, 2H, H(4”), H(6”)), 7.05 (d, *J* = 8.2, 2H, 2×H(*m*)), 6.82–6.72 (m, 1H, H(5”)), 6.71–6.65 (m, 1H, H(3”)), 5.72 (d, $^3J_{2,1'}$ = 10.8 Hz, 1H, H(2)), 5.41–5.17 (m, 1H, H(1’)), 5.14–5.06 (m, 1H, H(5’)), 5.06–4.87 (m, 1H, H(5)), 3.72 and 3.59 (both s, 2×3H, 2 $CO_2Me$), 3.69 (s, 3H, OMe), 2.84–2.72 (m, 2H, $CH_2$(4)), 2.34 (s, 3H, C(*p*)–Me), 2.18–1.99 (m, 2H, $CH_2$(4’)), 1.92–1.80 (m, 2H, $CH_2$(3’)), 1.88 (br.s, 1H, $CH_3$(9’)), 1.70 (br.s, 3H, $CH_3$(8’)), 1.62 (br.s, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 169.9 and 167.4 (2 COO), 155.7 (C(2”)), 142.3 (C(*p*)), 140.8 (C(2’)), 138.3 (C(*i*)), 131.8 (C(6’)), 129.5 (C(1”)), 128.6 (2×CH(*m*)), 128.5 and 128.2 (CH(4”) and CH(6”)), 127.5 (2×CH(*o*)), 123.8 (CH(5’)), 121.4 (CH(1’)), 120.3 (CH(5”)), 110.4 (CH(3”)), 63.2 (C(3)), 57.2 (CH(5)), 61.3 (CH(2)), 55.1 (OMe), 53.3 and 52.4 (2 $CO_2Me$), 38.8 ($CH_2$(4)), 40.0 ($CH_2$(3’)), 26.7 ($CH_2$(4’)), 25.6 ($CH_3$(8’)), 21.4 (C(*p*)–Me), 17.7 ($CH_3$(7’)), 16.5 ($CH_3$(9’)) ppm. *Z,cis*-**6c**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.34 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.21–7.11 (m, 2H, H(4”), H(6”)), 7.06 (d, *J* = 8.7 Hz, 2H, 2×H(*o’*)), 6.93–6.82 (m, 1H, H(5”)), 6.71–6.65 (m, 1H, H(3”)), 5.72 (d, $^3J_{2,1'}$ = 10.8 Hz, 1H, H(2)), 5.41–5.17 (m, 2H, H(1’), H(5’)), 5.06–4.87 (m, 1H, H(5)), 3.69 and 3.59 (both s, 2×3H, 2 $CO_2Me$), 3.69 (s, 3H, OMe), 2.84–2.72 (m, 2H, $CH_2$(4)), 2.34 (s, 3H, C(*p*)–Me), 2.31–2.18 (m, 3H, $CH_2$(3’), H(4’a)), 2.18–1.99 (m, 1H, H(4’b)), 1.78 (br.s, 1H, $CH_3$(9’)), 1.74 (br.s, 3H, $CH_3$(8’)), 1.71 (br.s, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 169.9 and 167.4 (2 COO), 155.7 (C(2”)), 142.3 (C(*p*)), 140.1 (C(2’)), 138.6 (C(*i*)), 131.9 (C(6’)), 129.5 (C(1”)), 128.5 (2×CH(*m*)), 128.5 and 128.2 (CH(4”) and CH(6”)), 127.5 (2×CH(*o*)), 124.2 (CH(5’)), 121.4 (CH(1’)), 120.3 (CH(5”)), 110.4 (CH(3”)), 63.1 (C(3)), 57.2 (CH(5)), 61.0 (CH(2)), 55.1 (OMe), 53.2 and 52.6 (2 $CO_2Me$), 38.8 ($CH_2$(4)), 32.3 ($CH_2$(3’)), 26.6 ($CH_2$(4’)), 25.7 ($CH_3$(8’)), 23.6 ($CH_3$(9’)), 21.4 (C(*p*)–Me), 17.6 ($CH_3$(7’)) ppm.

**Dimethyl 2-(2,6-dimethylhepta-1,5-dien-1-yl)-5-(5-methylfuran-2-yl)-1-tosylpyrrolidine-3,3-dicarboxylate (6e)**




The title compound was prepared according to the procedure *B* as a mixture of diastereomers, *cis* (*E/Z* 2.4:1)/*trans* (*E/Z* 1.9:1) 1.3:1, in 7 mg yield (20%). Eluent: petroleum ether/EtOAc 10:1. Yellowish thick oil, $R_f$ = 0.43 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{29}H_{38}NO_7S^+$ [M+H]$^+$ 544.2363, found 544.2353. *E,trans*-**6e**: $^1$H NMR (600.1 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.10 (d, *J* = 8.2 Hz, 2H, 2×H(*m*)), 6.05 (d, $^3J_{3'',4''}$ = 3.1 Hz, 1H, H(3”)), 5.65 (dq, $^3J_{3'',4''}$ = 3.1, $^4J_{4'',6''}$ = 1.0 Hz, 1H, H(4”)), 5.63 (d, $^3J_{2,1'}$ = 10.6 Hz, 1H, H(2)), 5.10–5.05 (m, 1H, H(5’)), 5.01 (dq, $^3J_{2,1'}$ = 10.6, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1’)), 4.95 (dd, $^3J_{4a,5}$ = 10.0, $^3J_{4b,5}$ = 2.1 Hz, 1H, H(5)), 3.68 and 3.61 (both s, 2×3H, 2 $CO_2Me$), 3.17 (dd, $^2J_{4a,4b}$ = 14.0, $^3J_{4a,5}$ = 10.0 Hz, 1H, $H_{syn}$(4a)), 2.58 (dd, $^2J_{4a,4b}$ = 14.0, $^3J_{4b,5}$ = 2.1 Hz, 1H, $H_{anti}$(4b)), 2.36 (s, 3H, C(*p*)–Me), 2.12–1.89 (m, 4H, $CH_2$(3’), $CH_2$(4’)), 1.95 (d, $^4J_{4'',6''}$ = 1.0 Hz, 3H, $CH_3$(6”)), 1.81 (d, $^4J_{1',9'}$ = 1.3 Hz, 1H, $CH_3$(9’)), 1.69 (br.s, 3H, $CH_3$(8’)), 1.60 (br.s, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): δ 169.7 and 167.5 (2 COO), 151.5 (C(5”)), 150.0 (C(2”)), 142.2 (C(*p*)), 141.8 (C(2’)), 138.0 (C(*i*)), 131.8 (C(6’)), 128.6 (2×CH(*m*)), 127.5 (2×CH(*o*)), 123.8 (CH(5’)), 119.4 (CH(1’)), 110.3 (CH(3”)), 105.9 (CH(4”)), 63.5 (C(3)), 62.2 (CH(2)), 53.9 (CH(5)), 52.8 and 52.7 (2 $CO_2Me$), 36.5 ($CH_2$(4)), 39.9 ($CH_2$(3’)), 26.4 ($CH_2$(4’)), 25.6 ($CH_3$(8’)), 21.4 (C(*p*)–Me), 17.7 ($CH_3$(7’)), 16.5 ($CH_3$(9’)), 13.2 ($CH_3$(6”)) ppm. *Z,trans*-**6e**: $^1$H NMR (600.1 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.11 (d, *J* = 8.2 Hz, 2H, 2×H(*m*)), 6.07 (d, $^3J_{3'',4''}$ = 3.1 Hz, 1H, H(3”)), 5.67 (dq, $^3J_{3'',4''}$ = 3.1, $^4J_{4'',6''}$ = 1.0 Hz, 1H, H(4”)), 5.68 (d, $^3J_{2,1'}$ = 10.7 Hz, 1H, H(2)), 5.25–5.20 (m, 1H, H(5’)), 4.94 (dd, $^3J_{4a,5}$ = 9.9, $^3J_{4b,5}$ = 2.3 Hz, 1H, H(5)), 4.91 (dq, $^3J_{2,1'}$ = 10.7, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1’)), 3.67 and 3.60 (both s, 2×3H, 2 $CO_2Me$), 3.15 (dd, $^2J_{4a,4b}$ = 13.9, $^3J_{4a,5}$ = 9.9 Hz, 1H, $H_{syn}$(4a)), 2.59 (dd, $^2J_{4a,4b}$ = 13.9, $^3J_{4b,5}$ = 2.3 Hz, 1H, $H_{anti}$(4b)), 2.36 (s, 3H, C(*p*)–Me), 2.31–2.13 (m, 3H, $CH_2$(3’), H(4’a)), 2.12–1.89 (m, 1H, H(4’b)), 1.97 (br.s, 3H, $CH_3$(6”)), 1.72 (br.s, 3H, $CH_3$(8’)), 1.67 (br.s, 3H, $CH_3$(7’)), 1.67 (d, $^4J_{1',9'}$ = 1.3 Hz, 1H, $CH_3$(9’)) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): δ 169.5 and 167.6 (2 COO), 151.5 (C(5”)), 150.1 (C(2”)), 142.2 (C(*p*)), 141.9 (C(2’)), 138.1 (C(*i*)), 131.9 (C(6’)), 128.6 (2×CH(*m*)), 127.6 (2×CH(*o*)), 124.4 (CH(5’)), 119.9 (CH(1’)), 110.2 (CH(3”)), 105.9 (CH(4”)), 63.7 (C(3)), 61.8 (CH(2)), 54.1 (CH(5)), 52.8 and 52.7 (2 $CO_2Me$), 36.6 ($CH_2$(4)), 32.3 ($CH_2$(3’)), 26.2 ($CH_2$(4’)), 25.7 ($CH_3$(8’)), 23.5 ($CH_3$(9’)), 21.4 (C(*p*)–Me), 17.7 ($CH_3$(7’)), 13.3 ($CH_3$(6”)) ppm. *E,cis*-**6e**: $^1$H NMR (600.1 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.01 (d, *J* = 8.2 Hz, 2H, 2×H(*m*)), 6.13 (d, $^3J_{3'',4''}$ = 3.1 Hz, 1H, H(3”)), 5.73 (dq, $^3J_{3'',4''}$ = 3.1, $^4J_{4'',6''}$ = 1.0 Hz, 1H, H(4”)), 5.71 (d, $^3J_{2,1'}$ = 10.6 Hz, 1H, H(2)), 5.19 (dq, $^3J_{2,1'}$ = 10.6, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1’)), 5.10–5.05 (m, 1H, H(5’)), 4.76 (dd, $^3J_{4a,5}$ = 11.0, $^3J_{4b,5}$ = 6.8 Hz, 1H, H(5)), 3.84 and 3.63 (both s, 2×3H, 2 $CO_2Me$), 3.01 (dd, $^2J_{4a,4b}$ = 13.7, $^3J_{4a,5}$ = 11.0 Hz, 1H, $H_{syn}$(4a)), 2.67 (dd, $^2J_{4a,4b}$ = 13.7, $^3J_{4b,5}$ = 6.8 Hz, 1H, $H_{anti}$(4b)), 2.32 (s, 3H, C(*p*)–Me), 2.12–1.89 (m, 4H, $CH_2$(3’), $CH_2$(4’)), 1.97 (br.s, 3H, $CH_3$(6”)), 1.83 (d, $^4J_{1',9'}$ = 1.3 Hz, 1H, $CH_3$(9’)), 1.69 (br.s, 3H, $CH_3$(8’)), 1.60 (br.s, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): δ 169.7 and 167.3 (2 COO), 152.1 (C(5”)), 148.5 (C(2”)), 141.9 (C(*p*)), 141.3 (C(2’)), 138.5 (C(*i*)), 131.8 (C(6’)), 128.4 (2×CH(*m*)), 127.1 (2×CH(*o*)), 123.8 (CH(5’)), 120.6 (CH(1’)), 110.9 (CH(3”)), 105.9 (CH(4”)), 62.9 (C(3)), 60.9 (CH(2)), 54.5 (CH(5)), 53.4 and 52.5 (2 $CO_2Me$), 37.1 ($CH_2$(4)), 39.7 ($CH_2$(3’)), 26.4 ($CH_2$(4’)), 25.6 ($CH_3$(8’)), 21.3 (C(*p*)–Me), 17.7 ($CH_3$(7’)), 16.6 ($CH_3$(9’)), 13.3 ($CH_3$(6”)) ppm. *Z,cis*-**6e**: $^1$H NMR (600.1 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.02 (d, *J* = 8.2 Hz, 2H, 2×H(*m*)), 6.12 (d, $^3J_{3'',4''}$ = 3.1 Hz, 1H, H(3”)), 5.73 (d, $^3J_{2,1'}$ = 10.6 Hz, 1H, H(2)), 5.72 (dq, $^3J_{3'',4''}$ = 3.1, $^4J_{4'',6''}$ = 1.0 Hz, 1H, H(4”)), 5.25–5.20 (m, 1H, H(5’)), 5.18 (dq, $^3J_{2,1'}$ = 10.6, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1’)), 4.71 (dd, $^3J_{4a,5}$ = 11.0, $^3J_{4b,5}$ = 6.8 Hz, 1H, H(5)), 3.82 and 3.63 (both s, 2×3H, 2 $CO_2Me$), 3.02 (dd, $^2J_{4a,4b}$ = 13.7, $^3J_{4a,5}$ = 11.0 Hz, 1H, $H_{syn}$(4a)), 2.67 (dd, $^2J_{4a,4b}$ = 13.7, $^3J_{4b,5}$ = 6.8 Hz, 1H, $H_{anti}$(4b)), 2.33 (s, 3H, C(*p*)–Me), 2.31–2.13 (m, 3H, $CH_2$(3’), H(4’a)), 2.12–1.89 (m, 1H, H(4’b)), 1.97 (br.s, 3H, $CH_3$(6”)), 1.72 (d, $^4J_{1',9'}$ = 1.3 Hz, 1H, $CH_3$(9’)), 1.69 (br.s, 3H, $CH_3$(8’)), 1.67 (br.s, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): δ 169.7 and 167.4 (2 COO), 152.1 (C(5”)), 148.4 (C(2”)), 141.9 (C(*p*)), 141.4 (C(2’)), 138.4 (C(*i*)), 132.0 (C(6’)), 128.4 (2×CH(*m*)), 127.1 (2×CH(*o*)), 124.2 (CH(5’)), 121.4 (CH(1’)), 110.9 (CH(3”)), 105.9 (CH(4”)), 63.0 (C(3)), 60.7 (CH(2)), 54.5 (CH(5)), 53.4 and 52.7 (2 $CO_2Me$), 37.2 ($CH_2$(4)), 32.2 ($CH_2$(3’)), 26.6 ($CH_2$(4’)), 25.7 ($CH_3$(8’)), 23.4 ($CH_3$(9’)), 21.3 (C(*p*)–Me), 17.6 ($CH_3$(7’)), 13.3 ($CH_3$(6”)) ppm.

**4-methyl-*N*-((1*RS*,6*SR*)-3-methyl-6-(prop-1-en-2-yl)cyclohex-2-en-1-yl)benzenesulfonamide (8)**




The title compound was prepared according to the procedure *B* in 7.5 mg yield (38%). Eluent: petroleum ether/EtOAc 15:1. Colorless solid, mp 123–125 °C, $R_f$ = 0.62 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{17}H_{23}NNaO_2S^+$ $[M+Na]^+$ 328.1342, found: 328.1346. $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.2 Hz, 2H, 2×H(*o*)), 7.28 (d, *J* = 8.2 Hz, 2H, 2×H(*m*)), 5.39 (m, 1H, H(2)), 4.70 (dq, $^2J_{2'a,2'b}$ = $^4J_{2'a,3'}$ = 1.6 Hz, 1H, H(2'a)), 4.66 (dq, $^2J_{2'a,2'b}$ = 1.6, $^4J_{2'b,3'}$ = 0.8 Hz, 1H, H(2'b)), 4.32 (d, *J* = 6.1 Hz, 1H, NH), 3.69–3.56 (m, 1H, CH(1)), 2.44 (s, 3H, C(*p*)–Me), 2.02 (ddd, $^3J_{5a,6}$ = 10.7, $^3J_{1,6}$ = 9.1, $^3J_{5b,6}$ = 3.7 Hz, 1H, CH(6)), 2.24–1.83 (m, 2H, $CH_2$(4)), 1.62 (br.s, 3H, $CH_3$(7)), 1.68–1.58 (m, 2H, $CH_2$(5)), 1.31 (dd, $^4J_{2'a,3'}$ = 1.6, $^4J_{2'b,3'}$ = 0.8 Hz, 3H, $CH_3$(3')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 145.4 (C(1')), 143.2 (C(*p*)), 137.4 (C(*i*)), 137.1 (C(3)), 129.4 (2×CH(*m*)), 127.4 (2×CH(*o*)), 122.6 (C(2)), 113.2 ($CH_2$(2')), 52.3 (CH(1)), 48.4 (CH(6)), 29.3 ($CH_2$(4)), 26.4 ($CH_2$(5)), 23.1 ($CH_3$(7)), 21.5 (C(*p*)–Me), 18.3 ($CH_3$(3')) ppm.

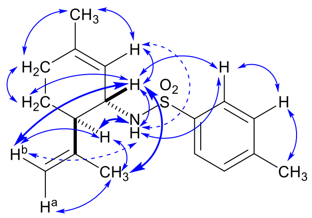
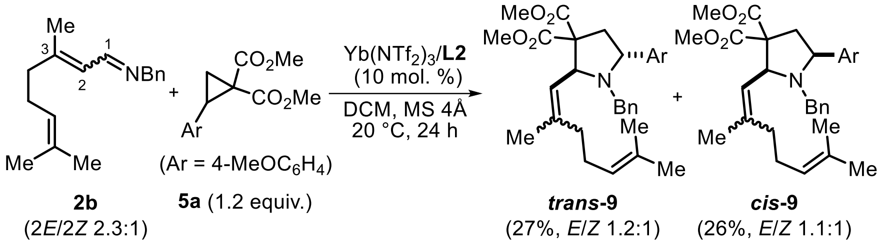


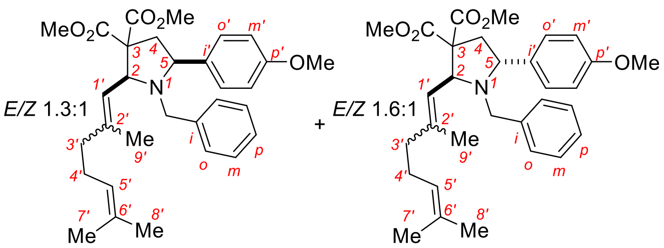

**Figure S3.** Key nOe interactions for **8** from the NOESY data

## 6. General synthetic procedure and spectroscopic data for *N*-benzylpyrrolidine 9




All operations were performed under dry argon atmosphere. A flame-dried vial was charged with a magnetic stirring bar, ligand **L2** (2.0 mg, 11 mol. %), $Yb(NTf_2)_3$ (8.4 mg, 10 mol. %), activated MS 4Å and 2 mL of dry DCM, followed by the ultrasonic irradiation for 1 h. After the preparation of catalytic complex, the DAC **5a** (29 mg, 0.108 mmol, 1.3 equiv.) and citral benzylimine **2b** (20 mg, 0.083 mmol) were dissolved in 1 ml of DCM and added to the catalyst at once. Then, the reaction mixture was stirred under conditions specified. After that, the reaction mixture was passed through a short pad of silica gel, the solvent was removed under reduced pressure. The residue was purified by column chromatography ($SiO_2$; petroleum ether/ethyl acetate 10:1) to afford title compound **9**.

**Dimethyl 1-benzyl-2-(2,6-dimethylhepta-1,5-dien-1-yl)-5-(4-methoxyphenyl)pyrrolidine-3,3-dicarboxylate (9)**




The title compound was prepared according to the general procedure as a mixture of diastereomers, *cis* (*E/Z* 1.3:1)/*trans* (*E/Z* 1.6:1) 1:1, in 22 mg yield (52%); NMR spectra presented for selected fraction *cis* (*E/Z* 3:1)/*trans* (*E/Z* 3.2:1) 1.1:1. Yellow thick oil, $R_f$ = 0.37 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{31}H_{40}NO_5^+$ $[M+H]^+$ 506.2901, found: 506.2913. *E,cis*-**9**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.7 Hz, 2H, 2×H(*o'*)), 7.35–7.23 (m, 2H, 2×H(*o*)), 7.22–7.07 (m, 3H, 2×H(*m*), H(*p*)), 6.89 (d, *J* = 8.7 Hz, 2H, 2×H(*m'*)), 5.19–5.00 (m, 1H, H(5')), 4.96 (dq, $^3J_{2,1'}$ = 9.8, $^4J_{1',9'}$ = 1.2 Hz, 1H, H(1')), 4.31 (d, $^3J_{2,1'}$ = 9.8 Hz, 1H, H(2)), 3.81 (s, 3H, OMe), 3.73 and 3.60 (both s, 2×3H, 2 $CO_2Me$), 3.73 and 3.48 (two doublets, $^2J_{HH}$ = 14.0 Hz, 2H, $CH_2$, Bn), 3.54 (dd, $^3J_{4a,5}$ = 10.9, $^3J_{4b,5}$ = 6.1 Hz, 1H, H(5)), 2.63 (dd, $^2J_{4a,4b}$ = 13.2, $^3J_{4a,5}$ = 10.9 Hz, 1H, $H_{syn}$(4a)), 2.38 (dd, $^2J_{4a,4b}$ = 13.2, $^3J_{4b,5}$ = 6.1 Hz, 1H, $H_{anti}$(4b)), 2.14–1.76 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.66 (br.s, 3H, $CH_3$(8')), 1.59 (br.s, 3H, $CH_3$(7')), 1.50 (d, $^4J_{1',9'}$ = 1.2 Hz, 1H, $CH_3$(9')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 172.2 and 169.9 (2 COO), 158.8 (C(*p'*)), 138.8 (C(2')), 138.0 (C(*i*)), 133.9 (C(*i'*)), 131.4 (C(6')), 129.5 (2×CH(*o*)), 128.9 (2×CH(*o'*)), 127.6 (2×CH(*m*)), 126.5 (CH(*p*)), 124.4 (CH(1')), 124.3 (CH(5')), 113.9 (2×CH(*m'*)), 65.5 (CH(5)), 64.5 (CH(2)), 63.0 (C(3)), 55.2 (OMe), 54.9 ($CH_2$, Bn), 52.7 and 52.0 (2 $CO_2Me$), 42.4 ($CH_2$(4)), 40.1 ($CH_2$(3')), 26.5 ($CH_2$(4')), 25.6 ($CH_3$(8')), 17.7 ($CH_3$(7')), 16.6 ($CH_3$(9')) ppm. *E,trans*-**9**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.7 Hz, 2H, 2×H(*o'*)), 7.35–7.23 (m, 2H, 2×H(*o*)), 7.22–7.07 (m, 3H, 2×H(*m*), H(*p*)), 6.85 (d, *J* = 8.7 Hz, 2H, 2×H(*m'*)), 5.14 (dq, $^3J_{2,1'}$ = 11.3, $^4J_{1',9'}$ = 1.2 Hz, 1H, H(1')), 5.19–5.00 (m, 1H, H(5')), 4.67 (d, $^3J_{2,1'}$ = 11.3 Hz, 1H, H(2)), 3.99 (dd, $^3J_{4a,5}$ = 9.4, $^3J_{4b,5}$ = 6.2 Hz, 1H, H(5)), 3.78 (s, 3H, OMe), 3.77 and 3.54 (both s, 2×3H, 2 $CO_2Me$), 3.54 and 3.34 (two doublets, $^2J_{HH}$ = 13.7 Hz, 2H, $CH_2$, Bn), 3.30 (dd, $^2J_{4a,4b}$ = 14.3, $^3J_{4a,5}$ = 9.4 Hz, 1H, $H_{syn}$(4a)), 2.26 (dd, $^2J_{4a,4b}$ = 14.3, $^3J_{4b,5}$ = 6.2 Hz, 1H, $H_{anti}$(4b)), 2.14–1.76 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.72 (br.s, 3H, $CH_3$(8')), 1.64 (br.s, 3H, $CH_3$(7')), 1.13 (d, $^4J_{1',9'}$ = 1.2 Hz, 1H, $CH_3$(9')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.9 and 169.4 (2 COO), 159.0 (C(*p'*)), 143.2 (C(2')), 139.5 (C(*i*)), 135.7 (C(*i'*)), 131.6 (C(6')), 128.4 and 128.3 (2×CH(*o*) and 2×CH(*o'*)), 127.9 (2×CH(*m*)), 126.4 (CH(*p*)), 124.1 (CH(5')), 116.1 (CH(1')), 113.8 (2×CH(*m'*)), 64.0 (CH(5)), 62.7 (C(3)), 61.2 (CH(2)), 55.2 (OMe), 52.7 and 52.2 (2 $CO_2Me$), 51.3 ($CH_2$, Bn), 40.5 ($CH_2$(4)), 39.7 ($CH_2$(3')), 26.6 ($CH_2$(4')), 25.7 ($CH_3$(8')), 17.8 ($CH_3$(7')), 15.6 ($CH_3$(9')) ppm. *Z,cis*-**9**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.6 Hz, 2H, 2×H(*o'*)), 7.35–7.23 (m, 2H, 2×H(*o*)), 7.22–7.07 (m, 3H, 2×H(*m*), H(*p*)), 6.85 (d, *J* = 8.6 Hz, 2H, 2×H(*m'*)), 5.19–5.00 (m, 1H, H(5')), 5.00–4.92 (m, 1H, H(1')), 4.41 (d, $^3J_{2,1'}$ = 10.0 Hz, 1H, H(2)), 3.79 (s, 3H, OMe), 3.77 and 3.60 (both s, 2×3H, 2 $CO_2Me$), 3.73 and 3.50 (two doublets, $^2J_{HH}$ = 13.9 Hz, 2H, $CH_2$, Bn), 3.60–3.49 (m, 1H, H(5)), 2.67 (dd, $^2J_{4a,4b}$ = 13.2, $^3J_{4a,5}$ = 11.3 Hz, 1H, $H_{syn}$(4a)), 2.37 (dd, $^2J_{4a,4b}$ = 13.2, $^3J_{4b,5}$ = 5.8 Hz, 1H, $H_{anti}$(4b)), 2.14–1.76 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.69 (br.s, 3H, $CH_3$(8')), 1.61 (br.s, 3H, $CH_3$(7')), 1.52 (d, $^4J_{1',9'}$ = 1.2 Hz, 1H, $CH_3$(9')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 172.0 and 169.9 (2 COO), 159.0 (C(*p'*)), 138.7 and 138.4 (C(2') and C(*i*)), 133.9 (C(*i'*)), 131.4 (C(6')), 129.2 (2×CH(*o*)), 128.9 (2×CH(*o'*)), 127.5 (2×CH(*m*)), 126.4 (CH(*p*)), 124.8 (CH(1')), 124.6 (CH(5')), 113.9 (2×CH(*m'*)), 65.8 (CH(5)), 64.0 (CH(2)), 63.2 (C(3)), 55.2 (OMe), 52.7 and 52.1 (2 $CO_2Me$), 51.3 ($CH_2$, Bn), 42.6 ($CH_2$(4)), 32.2 ($CH_2$(3')), 26.2 ($CH_2$(4')), 25.7 ($CH_3$(8')), 23.1 ($CH_3$(9')), 17.6 ($CH_3$(7')) ppm. *Z,trans*-**9**: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.35–7.23 (m, 4H, 2×H(*o*), 2×H(*o'*)), 7.22–7.07 (m, 3H, 2×H(*m*), H(*p*)), 6.83 (d, *J* = 8.8 Hz, 2H, 2×H(*m'*)), 5.19–5.00 (m, 1H, H(1')), 4.88–4.78 (m, 1H, H(5')), 4.80 (d, $^3J_{2,1'}$ = 11.1 Hz, 1H, H(2)), 4.05–3.94 (m, 1H, H(5)), 3.78 (s, 3H, OMe), 3.72 and 3.56 (both s, 2×3H, 2 $CO_2Me$), 3.54 and 3.40 (two doublets, $^2J_{HH}$ = 14.7 Hz, 2H, $CH_2$, Bn), 3.29 (dd, $^2J_{4a,4b}$ = 14.1, $^3J_{4a,5}$ = 9.2 Hz, 1H, $H_{syn}$(4a)), 2.27 (dd, $^2J_{4a,4b}$ = 14.1, $^3J_{4b,5}$ = 6.3 Hz, 1H, $H_{anti}$(4b)), 2.14–1.76 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.72 (d, $^4J_{1',9'}$ = 1.2 Hz, 1H, $CH_3$(9')), 1.60 (br.s, 3H, $CH_3$(8')), 1.44 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.9 and 169.4 (2 COO), 159.0 (C(*p'*)), 143.6 (C(2')), 139.6 (C(*i*)), 135.6 (C(*i'*)), 131.4 (C(6')), 128.4, 128.0 and 127.8 (2×CH(*o*), 2×CH(*m*) and 2×CH(*o'*)), 126.3 (CH(*p*)), 124.4 (CH(5')), 116.6 (CH(1')), 113.8 (2×CH(*m'*)), 64.0 (CH(5)), 63.0 (C(3)), 60.9 (CH(2)), 55.2 (OMe), 52.7 and 52.4 (2 $CO_2Me$), 50.9 ($CH_2$, Bn), 40.7 ($CH_2$(4)), 31.9 ($CH_2$(3')), 26.4 ($CH_2$(4')), 25.5 ($CH_3$(8')), 23.7 ($CH_3$(9')), 17.6 ($CH_3$(7')) ppm.

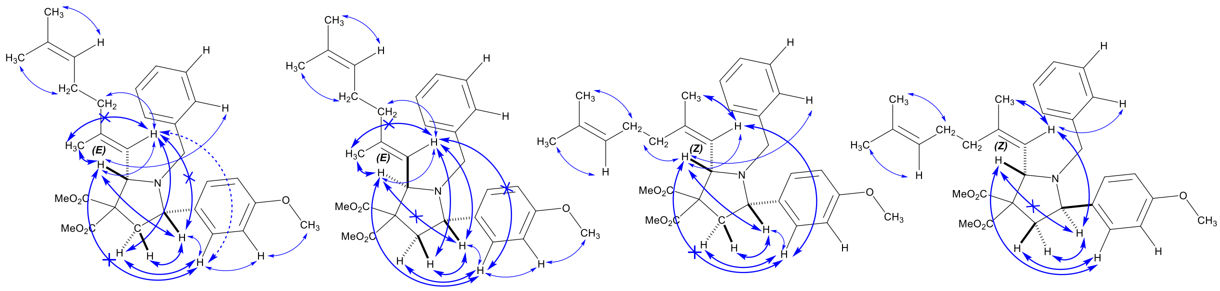
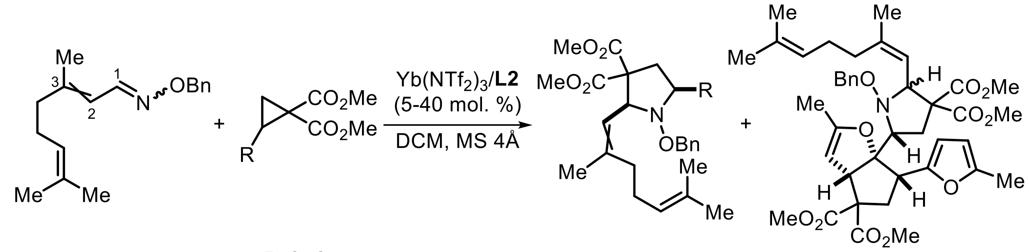


**Figure S4.** Key nOe interactions for the isomers of **9** from the NOESY data

## 7. General synthetic procedures and spectroscopic data for *N*-benzyloxypyrrolidines 10 and 2-oxabicyclo[3.3.0]oct-3-ene 11

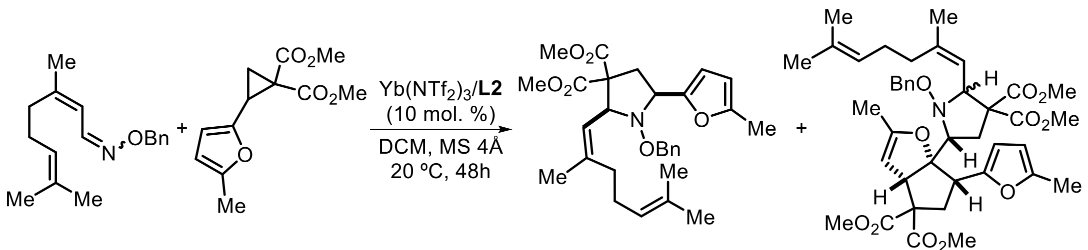



2*E*-**2c** (1*E*/1*Z* 1.2:1) or 2*Z*-**2c** (1*E*/1*Z* 2:1) | **5a,b,d–m** | *E*-**10a,b,d,f–m** or *Z*-**10a,d,e,k** (maj. diast.) | **11** (dr ~1:1, R = 2-MeFu)

(from 2*E*-**2c**): R = 4-MeOC$_6$H$_4$ (**a**), 3,4-(MeO)$_2$C$_6$H$_3$ (**b**), Ph (**d**), 4-MeC$_6$H$_4$ (**f**), 1-naphthyl (**g**), 4-FC$_6$H$_4$ (**h**), 3-BrC$_6$H$_4$ (**i**), 2-ClC$_6$H$_4$ (**j**), 4-MeCO$_2$C$_6$H$_4$ (**k**), 4-CNC$_6$H$_4$ (**l**), 4-NO$_2$C$_6$H$_4$ (**m**)
(from 2*Z*-**2c**): R = 4-MeOC$_6$H$_4$ (**a**), 5-MeFu (**e**), Ph (**d**), 4-MeCO$_2$C$_6$H$_4$ (**k**)

Procedure *A*: All operations were performed under dry argon atmosphere. A flame-dried vial was charged with a magnetic stirring bar, ligand **L2** (1.0–7.0 mg, 0.005–0.035 mmol, 6–42 mol. %), Yb(NTf$_2$)$_3$ (3.9–31.5 mg, 0.004–0.031 mmol, 5–40 mol. %), activated MS 4Å and 2 mL of dry DCM, followed by the ultrasonic irradiation for 1 h. After the preparation of catalytic complex, the DAC **5a,b,d,f–m** (1.4–2 equiv.) and *O*-benzyl oxime 2*E*- or 2*Z*-**2c** (20 mg, 0.078 mmol) were dissolved in 1 ml of DCM and added to the catalyst at once. Then, the reaction mixture was stirred under conditions specified. After that, the reaction mixture was passed through a short pad of silica gel, the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO$_2$, petroleum ether/ethyl acetate) to afford title compounds **10**.

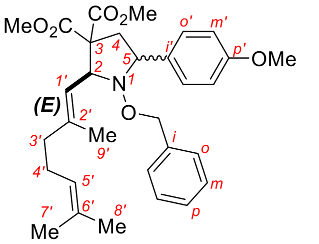
*Gram-scale synthetic procedure B for N-benzyloxypyrrolidine Z-***10a**: All operations were performed under dry argon atmosphere. A flame-dried flask was charged with a magnetic stirring bar, ligand **L2** (34 mg, 0.156 mmol, 5.5 mol. %), Yb(NTf$_2$)$_3$ (144 mg, 0.142 mmol, 5 mol. %), activated MS 4Å (0.5 g) and 50 mL of dry DCM, followed by the ultrasonic irradiation for 1 h. After the preparation of catalytic complex, the DAC **5a** (1.75 g, 6.6 mmol, 2.4 equiv.) and *O*-benzyl oxime 2*Z*-**2c** (0.73 g, 2.8 mmol) were dissolved in 20 ml of DCM and added to the catalyst at once. Then, the reaction mixture was stirred at room temperature over 3 days. After that, the reaction mixture was passed through a short pad of silica gel, the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO$_2$, petroleum ether/ethyl acetate 10:1) to afford title compound *Z*-**10a**.




2*Z*-**2c** (1*E*/1*Z* 2:1) | **5e** (1.1+1.1 equiv., *slow addition*) | *Z*-**10e** (*cis/trans* 2.9:1) | **11** (dr ~1:1)

*Synthetic procedure C for N-benzyloxypyrrolidine Z-***10e** *(slow addition)*: All operations were performed under dry argon atmosphere. A flame-dried flask equipped with a rubber septa and magnetic stirring bar, was charged with ligand **L2** (2.0 mg, 12 mol. %), Yb(NTf$_2$)$_3$ (7.8 mg, 10 mol. %), activated MS 4Å and 1 mL of dry DCM, followed by the ultrasonic irradiation for 1 h. After the preparation of catalytic complex, the solution of *O*-benzyl oxime 2*Z*-**2c** (20 mg, 0.078 mmol) in 0.5 ml of DCM was added to the catalyst solution. Then, the solution of **5e** (20 mg, 0.085 mmol, 1.1 equiv.) in 2.5 ml of DCM was slowly added to the mixture using a syringe pump over 5 hours (0.5 ml/h) followed by stirring overnight. Next day the second portion of **5e** (20 mg, 0.085 mmol, 1.1 equiv.) in 3 ml of DCM was slowly added to the mixture using a syringe pump over 10 hours (0.3 ml/h). After that, the reaction mixture was passed through a short pad of silica gel, the solvent was removed under reduced pressure. The residue was purified by column chromatography ($SiO_2$; petroleum ether/ethyl acetate 10:1→4:1) to afford title compounds *Z*-**10e** and **11**.

**Dimethyl 1-(benzyloxy)-2-((*E*)-2,6-dimethylhepta-1,5-dien-1-yl)-5-(4-methoxyphenyl)pyrrolidine-3,3-dicarboxylate (*E*-10a)**




The title compound was prepared according to the procedure *A* from 2*E*-**2c**, **5a** (42 mg, 0.156 mmol, 2 equiv.), Yb($NTf_2$)$_3$ (3.9 mg, 0.004 mmol, 5 mol.%), **L2** (1.0 mg, 0.005 mmol, 6 mol.%) at 20 °C, 48 h as a mixture of diastereomers, *cis*/*trans* 6.5:1, in 37 mg yield (91%; dr of isolated fraction: 6.7:1). Eluent: petroleum ether/EtOAc 10:1. Colorless thick oil, $R_f$ = 0.65 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{31}H_{40}NO_6^+$ [M+H]$^+$ 522.2850, found: 522.2843. *E,cis*-**10a**, major: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.7 Hz, 2H, 2×H(*o'*)), 7.20–7.13 (m, 3H, 2×H(*m*), H(*p*)), 6.98–6.88 (m, 2H, 2×H(*o*)), 6.89 (d, *J* = 8.7 Hz, 2H, 2×H(*m'*)), 5.20 (dq, $^3J_{2,1'}$ = 9.8 Hz, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 5.16–5.08 (m, 1H, H(5')), 4.62 (d, $^3J_{2,1'}$ = 9.8 Hz, 1H, H(2)), 4.47 and 4.17 (two doublets, $^2J_{HH}$ = 10.0 Hz, 2H, $CH_2$, Bn), 3.87 (dd, $^3J_{4a,5}$ = 11.5, $^3J_{4b,5}$ = 7.4 Hz, 1H, H(5)), 3.82 (s, 3H, OMe), 3.75 and 3.73 (both s, 2×3H, 2 $CO_2Me$), 2.80 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 11.5 Hz, 1H, $H_{syn}$(4a)), 2.46 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4b,5}$ = 7.4 Hz, 1H, $H_{anti}$(4b)), 2.21–1.95 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.83 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.65 (br.s, 3H, $CH_3$(8')), 1.60 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.6 and 170.3 (2 COO), 159.2 (C(*p'*)), 141.8 (C(2')), 137.1 (C(*i*)), 132.4 (C(*i'*)), 131.6 (C(6')), 129.3 (2×CH(*o'*)), 128.7 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.6 (CH(*p*)), 124.0 (CH(5')), 121.3 (CH(1')), 113.6 (2×CH(*m'*)), 77.1 ($CH_2$, Bn), 68.7 (CH(2)), 68.6 (CH(5)), 59.5 (C(3)), 55.2 (OMe), 52.8 and 52.3 (2 $CO_2Me$), 40.0 ($CH_2$(3')), 37.9 ($CH_2$(4)), 26.5 ($CH_2$(4')), 25.6 ($CH_3$(8')), 17.6 ($CH_3$(7')), 16.9 ($CH_3$(9')) ppm. *E,trans*-**10a**, minor: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.7 Hz, 2H, 2×H(*o'*)), 7.24–7.21 (m, 2H, 2×H(*m*)), 7.21–7.12 (m, 1H, H(*p*)), 7.14–7.09 (m, 2H, 2×H(*o*)), 6.85 (d, *J* = 8.7 Hz, 2H, 2×H(*m'*)), 5.29–5.16 (m, 1H, H(1')), 5.16–5.04 (m, 2H, H(2), H(5')), 4.38 and 4.34 (two doublets, $^2J_{HH}$ = 11.3 Hz, 2H, $CH_2$, Bn), 4.40–4.31 (m, 1H, H(5)), 3.80 (s, 3H, OMe), 3.74 and 3.60 (both s, 2×3H, 2 $CO_2Me$), 3.05 (dd, $^2J_{4a,4b}$ = 13.7, $^3J_{4a,5}$ = 8.3 Hz, 1H, $H_{syn}$(4a)), 2.38–2.26 (m, 1H, $H_{anti}$(4b)), 2.21–1.95 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.67 (br.s, 3H, $CH_3$(8')), 1.61 (m, 3H, $CH_3$(9')), 1.60 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.4 and 169.7 (2 COO), 158.9 (C(*p'*)), 142.1 (C(2')), 137.7 (C(*i*)), 132.1 (C(*i'*)), 131.5 (C(6')), 129.2 (2×CH(*o'*)), 128.8 (2×CH(*o*)), 127.9 (2×CH(*m*)), 127.4 (CH(*p*)), 123.9 (CH(5')), 118.1 (CH(1')), 113.5 (2×CH(*m'*)), 75.6 ($CH_2$, Bn), 68.7 (CH(2)), 67.4 (CH(5)), 62.3 (C(3)), 55.2 (OMe), 52.8 and 52.3 (2 $CO_2Me$), 40.0 ($CH_2$(3')), 36.6 ($CH_2$(4)), 26.7 ($CH_2$(4')), 25.6 ($CH_3$(8')), 17.6 ($CH_3$(7')), 16.4 ($CH_3$(9')) ppm.

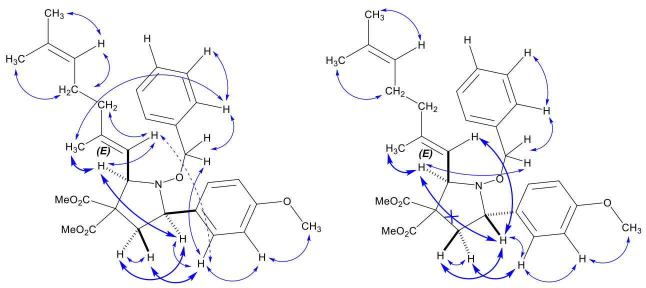
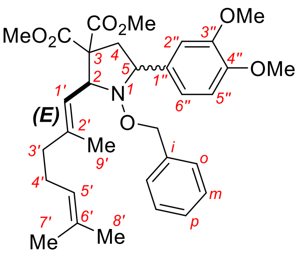


**Figure S5.** Key nOe interactions for the isomers of *E*-**10a** from the NOESY data

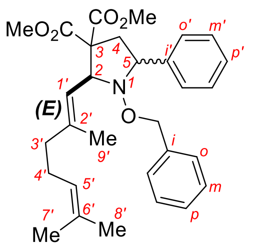
**Dimethyl 1-(benzyloxy)-5-(3,4-dimethoxyphenyl)-2-((*E*)-2,6-dimethylhepta-1,5-dien-1-yl)pyrrolidine-3,3-dicarboxylate (*E*-10b)**




The title compound was prepared according to the procedure *A* from 2*E*-**2c**, **5b** (46 mg, 0.156 mmol, 2 equiv.), Yb($NTf_2$)$_3$ (3.9 mg, 0.004 mmol, 5 mol.%), **L2** (1.0 mg, 0.005 mmol, 6 mol.%) at 20 °C, 48 h as a mixture of diastereomers, *cis*/*trans* 6.4:1, in 41 mg yield (95%; dr of isolated fraction: 6.7:1). Eluent: petroleum ether/EtOAc 5:1. Colorless thick oil, $R_f$ = 0.42 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{32}H_{42}NO_7^+$ [M+H]$^+$ 552.2956, found: 552.2952. *E,cis*-**10b**, major: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.20–7.14

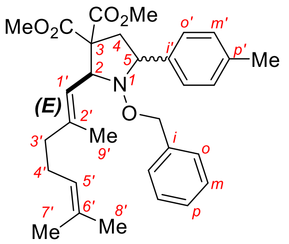
(m, 3H, 2×H(*m*), H(*p*)), 7.12 (d, $^4J_{2'',6''}$ = 1.9 Hz, 1H, H(2'')), 7.06 (dd, $^3J_{5'',6''}$ = 8.2 Hz, $^4J_{2'',6''}$ = 1.9 Hz, 1H, H(6'')), 6.98–6.88 (m, 2H, 2×H(*o*)), 6.85 (d, $^3J_{5'',6''}$ = 8.2 Hz, 1H, H(5'')), 5.21 (dq, $^3J_{2,1'}$ = 9.8 Hz, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 5.17–5.06 (m, 1H, H(5')), 4.63 (d, $^3J_{2,1'}$ = 9.8 Hz, 1H, H(2)), 4.50 and 4.20 (two doublets, $^2J_{HH}$ = 10.0 Hz, 2H, $CH_2$, Bn), 3.86 (dd, $^3J_{4a,5}$ = 11.4, $^3J_{4b,5}$ = 7.4 Hz, 1H, H(5)), 3.90 and 3.89 (both s, 2×3H, 2 OMe), 3.76 and 3.74 (both s, 2×3H, 2 $CO_2Me$), 2.81 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 11.4 Hz, 1H, $H_{syn}$(4a)), 2.47 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4b,5}$ = 7.4 Hz, 1H, $H_{anti}$(4b)), 2.21–1.97 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.84 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.65 (br.s, 3H, $CH_3$(8')), 1.60 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.5 and 170.3 (2 COO), 148.8 and 148.6 (C(3'') and C(4'')), 141.9 (C(2')), 137.1 (C(*i*)), 132.9 (C(1'')), 131.6 (C(6')), 128.7 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.6 (CH(*p*)), 124.0 (CH(5')), 121.2 (CH(1')), 120.4 (CH(6'')), 111.2 (CH(2'')), 110.7 (CH(5'')), 77.1 ($CH_2$, Bn), 68.9 (CH(5)), 68.8 (CH(2)), 59.5 (C(3)), 55.9 and 55.8 (2 OMe), 52.8 and 52.4 (2 $CO_2Me$), 40.0 ($CH_2$(3')), 37.8 ($CH_2$(4)), 26.5 ($CH_2$(4')), 25.6 ($CH_3$(8')), 17.6 ($CH_3$(7')), 16.9 ($CH_3$(9')) ppm. *E,trans*-**10b**, minor: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.24–7.21 (m, 2H, 2×H(*m*)), 7.20–7.14 (m, 1H, H(*p*)), 7.14–7.09 (m, 2H, 2×H(*o*)), 6.98–6.88 (m, 2H, H(2''), H(6'')), 6.81 (d, $^3J_{5'',6''}$ = 8.7 Hz, 1H, H(5'')), 5.29–5.16 (m, 1H, H(1')), 5.17–5.06 (m, 2H, H(2), H(5')), 4.42 and 4.38 (two doublets, $^2J_{HH}$ = 11.3 Hz, 2H, $CH_2$, Bn), 4.35 (dd, $^3J_{4b,5}$ = 9.4 Hz, $^3J_{4a,5}$ = 8.4, 1H, H(5)), 3.89 and 3.84 (both s, 2×3H, 2 OMe), 3.75 and 3.61 (both s, 2×3H, 2 $CO_2Me$), 3.06 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 8.4 Hz, 1H, $H_{syn}$(4a)), 2.39–2.30 (m, 1H, $H_{anti}$(4b)), 2.21–1.97 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.68 (br.s, 3H, $CH_3$(8')), 1.63 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.60 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.4 and 169.7 (2 COO), 148.8 (C(3'') and C(4'')), 142.2 (C(2')), 137.6 (C(*i*)), 132.9 (C(1'')), 131.6 (C(6')), 128.7 (2×CH(*o*)), 127.9 (2×CH(*m*)), 127.5 (CH(*p*)), 123.9 (CH(5')), 120.5 (CH(6'')), 118.0 (CH(1')), 111.2 (CH(2'')), 110.8 (CH(5'')), 75.6 ($CH_2$, Bn), 68.8 (CH(2)), 66.8 (CH(5)), 61.7 (C(3)), 55.8 and 55.7 (2 OMe), 52.8 and 52.4 (2 $CO_2Me$), 40.0 ($CH_2$(3')), 36.6 ($CH_2$(4)), 26.7 ($CH_2$(4')), 25.6 ($CH_3$(8')), 17.7 ($CH_3$(7')), 16.4 ($CH_3$(9')) ppm.

**Dimethyl 1-(benzyloxy)-2-((*E*)-2,6-dimethylhepta-1,5-dien-1-yl)-5-phenylpyrrolidine-3,3-dicarboxylate (*E*-10d)**



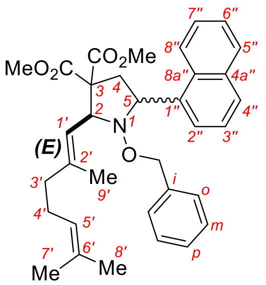

The title compound was prepared according to the procedure *A* from 2*E*-**2c**, **5d** (26 mg, 0.109 mmol, 1.4 equiv.), Yb(NTf$_2$)$_3$ (15.6 mg, 0.016 mmol, 20 mol.%), **L2** (3.7 mg, 0.018 mmol, 22 mol.%) at 20 °C, 48 h and 40 °C, 8 h as a mixture of diastereomers, *cis*/*trans* 6:1, in 36 mg yield (94%; dr of isolated fraction: 6.4:1). Eluent: petroleum ether/EtOAc 12:1. Colorless thick oil, $R_f$ = 0.67 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{30}H_{38}NO_5^+$ $[M+H]^+$ 492.2744, found: 492.2738. *E,cis*-**10d**, major: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.61–7.50 (m, 2H, 2×H(*o'*)), 7.42–7.27 (m, 3H, 2×H(*m'*), H(*p'*)), 7.20–7.12 (m, 3H, 2×H(*m*), H(*p*)), 6.95–6.85 (m, 2H, 2×H(*o*)), 5.22 (dq, $^3J_{2,1'}$ = 9.8 Hz, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 5.17–5.04 (m, 1H, H(5')), 4.64 (d, $^3J_{2,1'}$ = 9.8 Hz, 1H, H(2)), 4.49 and 4.17 (two doublets, $^2J_{HH}$ = 10.0 Hz, 2H, $CH_2$, Bn), 3.92 (dd, $^3J_{4a,5}$ = 11.5, $^3J_{4b,5}$ = 7.4 Hz, 1H, H(5)), 3.76 and 3.74 (both s, 2×3H, 2 $CO_2Me$), 2.82 (dd, $^2J_{4a,4b}$ = 13.7, $^3J_{4a,5}$ = 11.5 Hz, 1H, $H_{syn}$(4a)), 2.50 (dd, $^2J_{4a,4b}$ = 13.7, $^3J_{4b,5}$ = 7.4 Hz, 1H, $H_{anti}$(4b)), 2.20–1.97 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.83 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.65 (br.s, 3H, $CH_3$(8')), 1.60 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.6 and 170.3 (2 COO), 141.9 (C(2')), 140.4 (C(*i'*)), 137.0 (C(*i*)), 131.6 (C(6')), 128.7 (2×CH(*o*)), 128.3 and 128.2 (2×CH(*o'*) and 2×CH(*m'*)), 128.0 (2×CH(*m*)), 127.7 and 127.6 (CH(*p*) and CH(*p'*)), 124.0 (CH(5')), 121.3 (CH(1')), 77.2 ($CH_2$, Bn), 69.2 (CH(5)), 68.9 (CH(2)), 59.6 (C(3)), 52.8 and 52.4 (2 $CO_2Me$), 40.1 ($CH_2$(3')), 38.0 ($CH_2$(4)), 26.5 ($CH_2$(4')), 25.6 ($CH_3$(8')), 17.7 ($CH_3$(7')), 17.0 ($CH_3$(9')) ppm. *E,trans*-**10d**, minor: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.42–7.27 (m, 5H, 2×H(*o'*), 2×H(*m'*), H(*p'*)), 7.24–7.19 (m, 3H, 2×H(*m*), H(*p*)), 7.13–7.07 (m, 2H, 2×H(*o*)), 5.28–5.17 (m, 1H, H(1')), 5.17–5.04 (m, 2H, H(2), H(5')), 4.39 and 4.37 (two doublets, $^2J_{HH}$ = 11.3 Hz, 2H, $CH_2$, Bn), 4.42–4.35 (m, 1H, H(5)), 3.74 and 3.60 (both s, 2×3H, 2 $CO_2Me$), 3.10 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 8.4 Hz, 1H, $H_{syn}$(4a)), 2.38–2.30 (m, 1H, $H_{anti}$(4b)), 2.20–1.97 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.68 (br.s, 3H, $CH_3$(8')), 1.63–1.57 (m, 6H, $CH_3$(7'), $CH_3$(9')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.4 and 169.7 (2 COO), 142.3 (C(2')), 140.0 (C(*i'*)), 137.8 (C(*i*)), 131.6 (C(6')), 128.9 (2×CH(*o*)), 128.3 and 128.2 (2×CH(*o'*) and 2×CH(*m'*)), 128.0 (2×CH(*m*)), 127.5 and 127.3 (CH(*p*) and CH(*p'*)), 123.9 (CH(5')), 118.0 (CH(1')), 75.7 ($CH_2$, Bn), 68.9 (CH(2)), 67.2 (CH(5)), 62.4 (C(3)), 52.8 and 52.4 (2 $CO_2Me$), 40.0 ($CH_2$(3')), 36.6 ($CH_2$(4)), 26.7 ($CH_2$(4')), 25.6 ($CH_3$(8')), 17.0 ($CH_3$(7')), 16.4 ($CH_3$(9')) ppm.

**Dimethyl 1-(benzyloxy)-2-((*E*)-2,6-dimethylhepta-1,5-dien-1-yl)-5-(*p*-tolyl)pyrrolidine-3,3-dicarboxylate (*E*-10f)**



The title compound was prepared according to the procedure *A* from 2*E*-**2c**, **5f** (27 mg, 0.109 mmol, 1.4 equiv.), Yb(NTf$_2$)$_3$ (7.8 mg, 0.008 mmol, 10 mol.%), **L2** (1.8 mg, 0.009 mmol, 11 mol.%) at 20 °C, 48 h as a mixture of diastereomers, *cis*/*trans* 6.2:1, in 37 mg yield (95%; dr of isolated fraction: 6.7:1). Eluent: petroleum ether/EtOAc 10:1. Colorless thick oil, R$_f$ = 0.69 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{31}H_{40}NO_5^+$ [M+H]$^+$ 506.2901, found: 506.2905. *E,cis*-**10f**, major: $^1$H NMR (300.1 MHz, CDCl$_3$): δ 7.43 (d, *J* = 8.0 Hz, 2H, 2×H(*o'*)), 7.20–7.09 (m, 5H, 2×H(*m*), H(*p*), 2×H(*m'*)), 6.98–6.88 (m, 2H, 2×H(*o*)), 5.21 (dq, $^3J_{2,1'}$ = 9.8 Hz, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 5.17–5.03 (m, 1H, H(5')), 4.63 (d, $^3J_{2,1'}$ = 9.8 Hz, 1H, H(2)), 4.48 and 4.19 (two doublets, $^2J_{HH}$ = 10.0 Hz, 2H, CH$_2$, Bn), 3.89 (dd, $^3J_{4a,5}$ = 11.5, $^3J_{4b,5}$ = 7.4 Hz, 1H, H(5)), 3.75 and 3.73 (both s, 2×3H, 2 CO$_2$Me), 2.80 (dd, $^2J_{4a,4b}$ = 13.7, $^3J_{4a,5}$ = 11.5 Hz, 1H, H$_{syn}$(4a)), 2.47 (dd, $^2J_{4a,4b}$ = 13.7, $^3J_{4b,5}$ = 7.4 Hz, 1H, H$_{anti}$(4b)), 2.36 (s, 3H, C(*p'*)–Me), 2.17–1.99 (m, 4H, CH$_2$(3'), CH$_2$(4')), 1.82 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, CH$_3$(9')), 1.65 (br.s, 3H, CH$_3$(8')), 1.60 (br.s, 3H, CH$_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 171.6 and 170.3 (2 COO), 141.8 (C(2')), 137.3 and 137.3 (C(*i'*), C(*p'*)), 137.1 (C(*i*)), 131.6 (C(6')), 128.9 (2×CH(*m'*)), 128.7 (2×CH(*o*)), 128.1 (2×CH(*o'*)), 127.9 (2×CH(*m*)), 127.5 (CH(*p*)), 124.0 (CH(5')), 121.3 (CH(1')), 77.1 (CH$_2$, Bn), 68.9 (CH(5)), 68.8 (CH(2)), 59.6 (C(3)), 52.8 and 52.3 (2 CO$_2$Me), 40.0 (CH$_2$(3')), 38.0 (CH$_2$(4)), 26.5 (CH$_2$(4')), 25.6 (CH$_3$(8')), 21.1 (C(*p'*)–Me), 17.6 (CH$_3$(7')), 17.0 (CH$_3$(9')) ppm. *E,trans*-**10f**, minor: $^1$H NMR (300.1 MHz, CDCl$_3$): δ 7.29 (d, *J* = 8.0 Hz, 2H, 2×H(*o'*)), 7.23–7.21 (m, 2H, 2×H(*m*)), 7.21–7.09 (m, 5H, H(*p*), 2×H(*o*), 2×H(*m'*)), 5.28–5.17 (m, 1H, H(1')), 5.16–5.04 (m, 2H, H(2), H(5')), 4.39 and 4.37 (two doublets, $^2J_{HH}$ = 11.3 Hz, 2H, CH$_2$, Bn), 4.41–4.33 (m, 1H, H(5)), 3.73 and 3.59 (both s, 2×3H, 2 CO$_2$Me), 3.07 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 8.4 Hz, 1H, H$_{syn}$(4a)), 2.34 (s, 3H, C(*p'*)–Me), 2.39–2.31 (m, 1H, H$_{anti}$(4b)), 2.17–1.99 (m, 4H, CH$_2$(3'), CH$_2$(4')), 1.67 (br.s, 3H, CH$_3$(8')), 1.60 (br.s, 6H, CH$_3$(7'), CH$_3$(9')) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 171.4 and 169.8 (2 COO), 142.1 (C(2')), 137.6 and 137.7 (C(*i*), C(*i'*)), 136.9 (C(*p'*)), 131.5 (C(6')), 128.1 (2×CH(*o'*)), 128.8 (2×CH(*o*), 2×CH(*m'*)), 127.9 (2×CH(*m*), 2×CH(*o'*)), 127.4 (CH(*p*)), 123.9 (CH(5')), 118.0 (CH(1')), 75.7 (CH$_2$, Bn), 68.7 (CH(2)), 67.5 (CH(5)), 62.4 (C(3)), 52.8 and 52.3 (2 CO$_2$Me), 40.0 (CH$_2$(3')), 36.6 (CH$_2$(4)), 26.7 (CH$_2$(4')), 25.6 (CH$_3$(8')), 21.1 (C(*p'*)–Me), 17.7 (CH$_3$(7')), 16.4 (CH$_3$(9')) ppm.

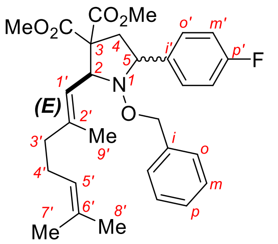
**Dimethyl 1-(benzyloxy)-2-((*E*)-2,6-dimethylhepta-1,5-dien-1-yl)-5-(naphthalen-1-yl)pyrrolidine-3,3-dicarboxylate (*E*-10g)**



The title compound was prepared according to the procedure *A* from 2*E*-**2c**, **5g** (35 mg, 0.125 mmol, 1.6 equiv.), Yb(NTf$_2$)$_3$ (7.8 mg, 0.008 mmol, 10 mol.%), **L2** (1.8 mg, 0.009 mmol, 11 mol.%) at 20 °C, 48 h and 40 °C, 24 h as a mixture of diastereomers, *cis*/*trans* 4.1:1, in 38 mg yield (91%; dr of isolated fraction: 4.2:1). Eluent: petroleum ether/EtOAc 13:1. Colorless thick oil, R$_f$ = 0.57 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{34}H_{40}NO_5^+$ [M+H]$^+$ 542.2901; found: 542.2902. *E,cis*-**10g**, major: $^1$H NMR (300.1 MHz, CDCl$_3$): δ 8.37 (d, $^3J_{7'',8''}$ = 7.8 Hz, 1H, H(8'')), 7.96 (d, $^3J_{2'',3''}$ = 7.1 Hz, 1H, H(2'')), 7.90–7.83 (m, 1H, H(5'')), 7.80 (d, $^3J_{3'',4''}$ = 8.2 Hz, 1H, H(4'')), 7.54–7.40 (m, 3H, H(3''), H(6''), H(7'')), 7.12–6.99 (m, 3H, 2×H(*m*), H(*p*)), 6.85–6.74 (m, 2H, 2×H(*o*)), 5.36 (dq, $^3J_{2,1'}$ = 9.8 Hz, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 5.20–5.10 (m, 1H, H(5')), 4.77 (dd, $^3J_{4a,5}$ = 11.3 Hz, $^3J_{4b,5}$ = 7.9, 1H, H(5)), 4.76 (d, $^3J_{2,1'}$ = 9.8 Hz, 1H, H(2)), 4.59 and 4.33 (two doublets, $^2J_{HH}$ = 10.1 Hz, 2H, CH$_2$, Bn), 3.79 and 3.75 (both s, 2×3H, 2 CO$_2$Me), 2.89 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 11.3 Hz, 1H, H$_{syn}$(4a)), 2.52 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4b,5}$ = 7.9 Hz, 1H, H$_{anti}$(4b)), 2.23–2.00 (m, 4H, CH$_2$(3'), CH$_2$(4')), 1.87 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, CH$_3$(9')), 1.66 (br.s, 3H, CH$_3$(8')), 1.62 (br.s, 3H, CH$_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 171.6 and 170.3 (2 COO), 142.0 (C(2')), 137.0 (C(*i*)), 136.2 (C(1'')), 133.8 (C(4a'')), 131.8 (C(8a'')), 131.6 (C(6')), 128.7 (CH(5'')), 128.5 (2×CH(*o*)), 128.0 (CH(4'')), 127.9 (2×CH(*m*)), 127.5 (CH(*p*)), 125.7 (CH(7'')), 125.5 (br.s, CH(2'')), 125.5 (CH(3'')), 125.4 (CH(6'')), 124.0 (CH(5')), 123.8 (br.s, CH(8'')), 121.3 (CH(1')), 77.0 (CH$_2$, Bn), 69.4 (CH(2)), 66.4 (br.s, CH(5)), 59.9 (C(3)), 52.9 and 52.4 (2 CO$_2$Me), 40.1 (CH$_2$(3')), 37.9 (CH$_2$(4)), 26.5 (CH$_2$(4')), 25.6 (CH$_3$(8')), 17.7 (CH$_3$(7')), 17.0 (CH$_3$(9')) ppm. *E,trans*-**10g**, minor: $^1$H NMR (300.1 MHz, CDCl$_3$): δ 8.27 (d, $^3J_{7'',8''}$ = 7.9

Hz, 1H, H(8")), 7.90–7.83 (m, 1H, H(5")), 7.82–7.75 (m, 1H, H(4")), 7.67 (d, $^3J_{2",3"}$ = 7.1 Hz, 1H, H(2")), 7.54–7.40 (m, 3H, H(3"), H(6"), H(7")), 7.19–7.12 (m, 3H, 2×H(*m*), H(*p*)), 7.12–6.99 (m, 2H, 2×H(*o*)), 5.44–5.35 (m, 1H, H(1')), 5.23 (d, $^3J_{2,1'}$ = 10.4 Hz, 1H, H(2)), 5.20–5.10 (m, 2H, H(5), H(5')), 4.38 and 4.30 (two doublets, $^2J_{HH}$ = 11.4 Hz, 2H, CH$_2$, Bn), 3.72 and 3.63 (both s, 2×3H, 2 CO$_2$Me), 3.24 (dd, $^2J_{4a,4b}$ = 13.5, $^3J_{4a,5}$ = 8.3 Hz, 1H, H$_{syn}$(4a)), 2.62–2.48 (m, 1H, H$_{anti}$(4b)), 2.23–2.00 (m, 5H, CH$_2$(3'), CH$_2$(4')), 1.70 (br.s, 3H, CH$_3$(8')), 1.66 (m, 3H, CH$_3$(9')), 1.63 (br.s, 3H, CH$_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 171.4 and 170.9 (2 COO), 142.0 (C(2')), 137.6 (C(*i*)), 136.0 (C(1")), 133.8 (C(4a")), 131.8 (C(8a")), 131.7 (C(6')), 128.6 (CH(5")), 128.8 (2×CH(*o*)), 127.9 (2×CH(*m*)), 127.8 (CH(4")), 127.4 (CH(*p*)), 125.8, 125.4 and 125.3 (CH(3"), CH(6"), CH(7")), 124.4 (CH(2")), 124.1 (CH(8")), 124.0 (CH(5')), 118.4 (CH(1')), 75.5 (CH$_2$, Bn), 67.2 (CH(2)), 65.0 (CH(5)), 62.0 (C(3)), 52.8 and 52.4 (2 CO$_2$Me), 40.1 (CH$_2$(3')), 36.3 (CH$_2$(4)), 26.7 (CH$_2$(4')), 25.7 (CH$_3$(8')), 17.7 (CH$_3$(7')), 16.5 (CH$_3$(9')) ppm.

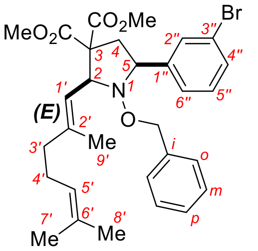
**Dimethyl 1-(benzyloxy)-2-((*E*)-2,6-dimethylhepta-1,5-dien-1-yl)-5-(4-fluorophenyl)pyrrolidine-3,3-dicarboxylate (*E*-10h)**




The title compound was prepared according to the procedure *A* from 2*E*-**2c**, **5h** (27 mg, 0.109 mmol, 1.4 equiv.), Yb(NTf$_2$)$_3$ (15.6 mg, 0.016 mmol, 20 mol.%), **L2** (3.7 mg, 0.018 mmol, 22 mol.%) at 20 °C, 48 h and 40 °C, 8 h as a mixture of diastereomers, *cis*/*trans* 6.4:1, in 36 mg yield (91%; dr of isolated fraction: 6.7:1). Eluent: petroleum ether/EtOAc 10:1. Colorless thick oil, R$_f$ = 0.68 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{30}H_{37}FNO_5^+$ [M+H]$^+$ 510.2650, found: 510.2640. *E,cis*-**10h**, major: $^1$H NMR (300.1 MHz, CDCl$_3$): δ 7.55–7.43 (m, 2H, 2×H(*o'*)), 7.20–7.13 (m, 3H, 2×H(*m*), H(*p*)), 7.07–6.96 (m, 2H, 2×H(*m'*)), 6.95–6.88 (m, 2H, 2×H(*o*)), 5.21 (dq, $^3J_{2,1'}$ = 9.8 Hz, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 5.16–5.05 (m, 1H, H(5')), 4.64 (d, $^3J_{2,1'}$ = 9.8 Hz, 1H, H(2)), 4.49 and 4.17 (two doublets, $^2J_{HH}$ = 10.1 Hz, 2H, CH$_2$, Bn), 3.90 (dd, $^3J_{4a,5}$ = 11.4, $^3J_{4b,5}$ = 7.5 Hz, 1H, H(5)), 3.76 and 3.74 (both s, 2×3H, 2 CO$_2$Me), 2.76 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 11.4 Hz, 1H, H$_{syn}$(4a)), 2.48 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4b,5}$ = 7.5 Hz, 1H, H$_{anti}$(4b)), 2.23–1.95 (m, 4H, CH$_2$(3'), CH$_2$(4')), 1.84 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, CH$_3$(9')), 1.65 (br.s, 3H, CH$_3$(8')), 1.60 (br.s, 3H, CH$_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 171.5 and 170.2 (2 COO), 162.4 (d, $^1J_{C,F}$ = 245.2 Hz, C(*p'*)), 142.0 (C(2')), 136.9 (C(*i*)), 136.2 (d, $^4J_{C,F}$ = 3.0 Hz, C(*i'*)), 131.7 (C(6')), 129.8 (d, $^3J_{C,F}$ = 8.1 Hz, 2×CH(*o'*)), 128.7 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.7 (CH(*p*)), 124.0 (CH(5')), 121.2 (CH(1')), 115.0 (d, $^2J_{C,F}$ = 21.5 Hz, 2×CH(*m'*)), 77.2 (CH$_2$, Bn), 68.9 (CH(2)), 68.5 (CH(5)), 59.5 (C(3)), 52.9 and 52.4 (2 CO$_2$Me), 40.1 (CH$_2$(3')), 38.0 (CH$_2$(4)), 26.5 (CH$_2$(4')), 25.6 (CH$_3$(8')), 17.7 (CH$_3$(7')), 17.0 (CH$_3$(9')) ppm. $^{19}$F NMR (282.5 MHz, CDCl$_3$): δ -115.0 (tt, $^3J_{H,F}$ = 8.7 Hz, $^4J_{H,F}$ = 5.4 Hz) ppm. *E,trans*-**10h**, minor: $^1$H NMR (300.1 MHz, CDCl$_3$): δ 7.37–7.29 (m, 2H, 2×H(*o'*)), 7.25–7.20 (m, 3H, 2×H(*m*), H(*p*)), 7.13–7.07 (m, 2H, 2×H(*o*)), 7.07–6.96 (m, 2H, 2×H(*m'*)), 5.27–5.17 (m, 1H, H(1')), 5.16–5.04 (m, 2H, H(2), H(5')), 4.38 and 4.35 (two doublets, $^2J_{HH}$ = 11.3 Hz, 2H, CH$_2$, Bn), 4.41–4.32 (m, 1H, H(5)), 3.75 and 3.61 (both s, 2×3H, 2 CO$_2$Me), 3.08 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 8.4 Hz, 1H, H$_{syn}$(4a)), 2.38–2.30 (m, 1H, H$_{anti}$(4b)), 2.23–1.95 (m, 4H, CH$_2$(3'), CH$_2$(4')), 1.68 (br.s, 3H, CH$_3$(8')), 1.62 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, CH$_3$(9')), 1.57 (br.s, 3H, CH$_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 171.3 and 169.6 (2 COO), 162.0 (d, $^1J_{C,F}$ = 241.6 Hz, C(*p'*)), 142.8 (C(2')), 137.5 (C(*i*)), 137.0 (C(*i'*)), 131.6 (C(6')), 129.6 (d, $^3J_{C,F}$ = 8.2 Hz, 2×CH(*o'*)), 128.9 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.6 (CH(*p*)), 123.9 (CH(5')), 117.5 (CH(1')), 114.9 (d, $^2J_{C,F}$ = 21.5 Hz, 2×CH(*m'*)), 75.6 (CH$_2$, Bn), 68.9 (CH(2)), 67.1 (CH(5)), 62.7 (C(3)), 52.9 and 52.4 (2 CO$_2$Me), 40.1 (CH$_2$(3')), 36.6 (CH$_2$(4)), 26.7 (CH$_2$(4')), 25.6 (CH$_3$(8')), 17.7 (CH$_3$(7')), 16.4 (CH$_3$(9')) ppm. $^{19}$F NMR (282.5 MHz, CDCl$_3$): δ -115.5 (tt, $^3J_{H,F}$ = 8.7 Hz, $^4J_{H,F}$ = 5.5 Hz) ppm.

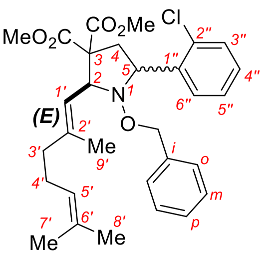
**Dimethyl 1-(benzyloxy)-5-(3-bromophenyl)-2-((*E*)-2,6-dimethylhepta-1,5-dien-1-yl)pyrrolidine-3,3-dicarboxylate (*E*-10i)**

The title compound was prepared according to the procedure *A* from 2*E*-**2c**, **5i** (39 mg, 0.125 mmol, 1.6 equiv.), Yb(NTf$_2$)$_3$ (15.6 mg, 0.016 mmol, 20 mol.%), **L2** (3.7 mg, 0.018 mmol, 22 mol.%) at 40 °C, 48 h as a mixture of diastereomers, *cis*/*trans* 5.3:1, in 38 mg yield (86%; dr of isolated fraction: 5.3:1). Eluent: petroleum ether/EtOAc 13:1. Colorless thick oil, R$_f$ = 0.58 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*:



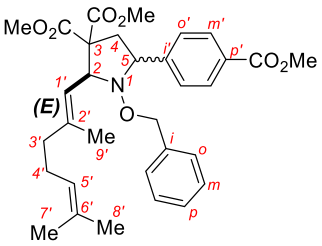
calcd for $C_{30}H_{37}BrNO_5^+$ $[M+H]^+$ 570.1850; found: 570.1850. *E,cis*-**10i**, major: $^{1}$H NMR (300.1 MHz, $CDCl_3$): δ 7.68 (t, $^{4}J_{2'',4''} = {}^{4}J_{2'',6''} = 1.8$ Hz, 1H, H(2”)), 7.47–7.37 (m, 2H, H(4”), H(6”)), 7.27–7.14 (m, 4H, 2×H(*m*), H(*p*), H(5”)), 6.98–6.88 (m, 2H, 2×H(*o*)), 5.22 (dq, $^{3}J_{2,1'} = 9.8$ Hz, $^{4}J_{1',9'} = 1.3$ Hz, 1H, H(1’)), 5.17–5.05 (m, 1H, H(5’)), 4.65 (d, $^{3}J_{2,1'} = 9.8$ Hz, 1H, H(2)), 4.53 and 4.22 (two doublets, $^{2}J_{HH} = 10.1$ Hz, 2H, $CH_2$, Bn), 3.88 (dd, $^{3}J_{4a,5} = 11.4$, $^{3}J_{4b,5} = 7.5$ Hz, 1H, H(5)), 3.76 and 3.74 (both s, 2×3H, 2 $CO_2Me$), 2.75 (dd, $^{2}J_{4a,4b} = 13.8$, $^{3}J_{4a,5} = 11.4$ Hz, 1H, $H_{syn}$(4a)), 2.49 (dd, $^{2}J_{4a,4b} = 13.8$, $^{3}J_{4b,5} = 7.5$ Hz, 1H, $H_{anti}$(4b)), 2.21–1.97 (m, 4H, $CH_2$(3’), $CH_2$(4’)), 1.83 (d, $^{4}J_{1',9'} = 1.3$ Hz, 3H, $CH_3$(9’)), 1.65 (br.s, 3H, $CH_3$(8’)), 1.61 (br.s, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.4 and 170.1 (2 COO), 142.9 (C(1”)), 142.1 (C(2’)), 136.9 (C(*i*)), 131.7 (C(6’)), 131.3 (CH(2”)), 130.8 (CH(4”)), 129.8 (CH(5”)), 128.7 (2×CH(*o*)), 128.1 (2×CH(*m*)), 127.7 (CH(*p*)), 126.9 (CH(6”)), 123.9 (CH(5’)), 121.1 (CH(1’)), 122.3 (C(3”)), 77.2 ($CH_2$, Bn), 69.0 (CH(2)), 68.7 (CH(5)), 59.7 (C(3)), 52.9 and 52.5 (2 $CO_2Me$), 40.0 ($CH_2$(3’)), 37.9 ($CH_2$(4)), 26.5 ($CH_2$(4’)), 25.6 ($CH_3$(8’)), 17.7 ($CH_3$(7’)), 17.0 ($CH_3$(9’)) ppm. *E,trans*-**10i**, minor: $^{1}$H NMR (300.1 MHz, $CDCl_3$): δ 7.53 (t, $^{4}J_{2'',4''} = {}^{4}J_{2'',6''} = 1.8$ Hz, 1H, H(2”)), 7.47–7.37 (m, 1H, H(4”)), 7.29 (d, $^{3}J_{5'',6''} = 7.8$ Hz, 1H, H(6”)), 7.27–7.14 (m, 4H, 2×H(*m*), H(*p*), H(5”)), 7.14–7.09 (m, 2H, 2×H(*o*)), 5.29–5.16 (m, 1H, H(1’)), 5.17–5.05 (m, 2H, H(2), H(5’)), 4.42 and 4.39 (two doublets, $^{2}J_{HH} = 11.3$ Hz, 2H, $CH_2$, Bn), 4.35 (dd, $^{3}J_{4b,5} = 9.2$ Hz, $^{3}J_{4a,5} = 8.5$, 1H, H(5)), 3.75 and 3.61 (both s, 2×3H, 2 $CO_2Me$), 3.08 (dd, $^{2}J_{4a,4b} = 13.7$, $^{3}J_{4a,5} = 8.5$ Hz, 1H, $H_{syn}$(4a)), 2.35–2.26 (m, 1H, $H_{anti}$(4b)), 2.21–1.97 (m, 4H, $CH_2$(3’), $CH_2$(4’)), 1.68 (br.s, 3H, $CH_3$(8’)), 1.63 (d, $^{4}J_{1',9'} = 1.3$ Hz, 3H, $CH_3$(9’)), 1.61 (br.s, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.2 and 169.4 (2 COO), 142.9 (C(1”)), 142.5 (C(2’)), 137.3 (C(*i*)), 131.7 (C(6’)), 131.1 (CH(2”)), 130.4 (CH(4”)), 129.7 (CH(5”)), 128.9 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.7 (CH(*p*)), 126.7 (CH(6”)), 123.9 (CH(5’)), 122.3 (C(3”)), 117.6 (CH(1’)), 75.6 ($CH_2$, Bn), 69.0 (CH(2)), 67.2 (CH(5)), 61.5 (C(3)), 52.9 and 52.5 (2 $CO_2Me$), 40.1 ($CH_2$(3’)), 36.4 ($CH_2$(4)), 26.7 ($CH_2$(4’)), 25.6 ($CH_3$(8’)), 17.7 ($CH_3$(7’)), 16.5 ($CH_3$(9’)) ppm.

**Dimethyl 1-(benzyloxy)-5-(2-chlorophenyl)-2-((*E*)-2,6-dimethylhepta-1,5-dien-1-yl)pyrrolidine-3,3-dicarboxylate (*E*-10j)**



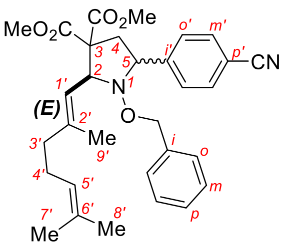
The title compound was prepared according to the procedure *A* from 2*E*-**2c**, **5j** (29 mg, 0.109 mmol, 1.4 equiv.), $Yb(NTf_2)_3$ (23.4 mg, 0.024 mmol, 30 mol.%), **L2** (5.9 mg, 0.029 mmol, 32 mol.%) at 40 °C, 48 h and 60 °C, 9 h as a mixture of diastereomers, *cis*/*trans* 5.2:1, in 37 mg yield (90%; dr of isolated fraction: 6.7:1). Eluent: petroleum ether/EtOAc 12:1. Colorless thick oil, $R_f = 0.60$ (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{30}H_{37}ClNO_5^+$ $[M+H]^+$ 526.2355; found: 526.2357. *E,cis*-**10j**, major: $^{1}$H NMR (300.1 MHz, $CDCl_3$): δ 7.93 (dd, $^{3}J_{5'',6''} = 7.7$ Hz, $^{4}J_{4'',6''} = 1.7$ Hz, 1H, H(6”)), 7.39–7.10 (m, 6H, 2×H(*m*), H(*p*), H(3”), H(4”), H(5”)), 7.03–6.94 (m, 2H, 2×H(*o*)), 5.25 (dq, $^{3}J_{2,1'} = 9.8$ Hz, $^{4}J_{1',9'} = 1.3$ Hz, 1H, H(1’)), 5.20–5.05 (m, 1H, H(5’)), 4.71 (d, $^{3}J_{2,1'} = 9.8$ Hz, 1H, H(2)), 4.64 and 4.44 (two doublets, $^{2}J_{HH} = 10.3$ Hz, 2H, $CH_2$, Bn), 4.58 (dd, $^{3}J_{4b,5} = 10.8$ Hz, $^{3}J_{4a,5} = 8.1$, 1H, H(5)), 3.77 and 3.72 (both s, 2×3H, 2 $CO_2Me$), 2.67 (dd, $^{2}J_{4a,4b} = 13.8$, $^{3}J_{4a,5} = 8.1$ Hz, 1H, $H_{syn}$(4a)), 2.52 (dd, $^{2}J_{4a,4b} = 13.8$, $^{3}J_{4b,5} = 10.8$ Hz, 1H, $H_{anti}$(4b)), 2.20–1.99 (m, 4H, $CH_2$(3’), $CH_2$(4’)), 1.84 (d, $^{4}J_{1',9'} = 1.3$ Hz, 3H, $CH_3$(9’)), 1.66 (br.s, 3H, $CH_3$(8’)), 1.61 (br.s, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.2 and 170.2 (2 COO), 142.0 (C(2’)), 138.7 (C(1”)), 137.2 (C(*i*)), 133.7 (C(2”)), 131.7 (C(6’)), 129.1 and 129.0 (CH(3”) and CH(6”)), 128.4 (2×CH(*o*)), 128.3 (CH(4”)), 128.0 (2×CH(*m*)), 127.6 (CH(*p*)), 126.9 (CH(5”)), 124.0 (CH(5’)), 121.2 (CH(1’)), 77.0 ($CH_2$, Bn), 69.0 (CH(2)), 65.0 (CH(5)), 59.8 (C(3)), 52.9 and 52.4 (2 $CO_2Me$), 40.1 ($CH_2$(3’)), 37.2 ($CH_2$(4)), 26.5 ($CH_2$(4’)), 25.6 ($CH_3$(8’)), 17.7 ($CH_3$(7’)), 17.0 ($CH_3$(9’)) ppm. *E,trans*-**10j**, minor: $^{1}$H NMR (300.1 MHz, $CDCl_3$): δ 7.55 (m, 1H, H(6”)), 7.39–7.10 (m, 9H, 2×H(*o*), 2×H(*m*), H(*p*), H(3”), H(4”), H(5”), H(6”)), 5.34 (dq, $^{3}J_{2,1'} = 10.8$ Hz, $^{4}J_{1',9'} = 1.3$ Hz, 1H, H(1’)), 5.20–5.05 (m, 2H, H(2), H(5’)), 4.86 (dd, $^{3}J_{4a,5} = 9.3$, $^{3}J_{4b,5} = 8.2$ Hz, 1H, H(5)), 4.52 and 4.49 (two doublets, $^{2}J_{HH} = 11.3$ Hz, 2H, $CH_2$, Bn), 3.71 and 3.61 (both s, 2×3H, 2 $CO_2Me$), 3.08 (dd, $^{2}J_{4a,4b} = 13.9$, $^{3}J_{4a,5} = 9.3$ Hz, 1H, $H_{syn}$(4a)), 2.20–1.99 (m, 5H, $CH_2$(3’), $CH_2$(4’), $H_{anti}$(4b)), 1.67 (br.s, 3H, $CH_3$(8’)), 1.63 (d, $^{4}J_{1',9'} = 1.3$ Hz, 3H, $CH_3$(9’)), 1.61 (br.s, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.1 and 169.1 (2 COO), 142.5 (C(2’)), 138.7 (C(1”)), 137.5 (C(*i*)), 133.9 (C(2”)), 131.6 (C(6’)), 129.3 (CH(3”)), 128.9 (2×CH(*o*)), 128.2 (CH(4”), CH(6”)), 128.0 (2×CH(*m*)), 127.6 (CH(*p*)), 126.6 (CH(5”)), 123.9 (CH(5’)), 117.5 (CH(1’)), 75.5 ($CH_2$, Bn), 68.9 (CH(2)), 63.8 (CH(5)), 61.3 (C(3)), 52.8 and 52.5 (2 $CO_2Me$), 40.1 ($CH_2$(3’)), 35.4 ($CH_2$(4)), 26.7 ($CH_2$(4’)), 25.6 ($CH_3$(8’)), 17.7 ($CH_3$(7’)), 16.4 ($CH_3$(9’)) ppm.

**Dimethyl 1-(benzyloxy)-2-((*E*)-2,6-dimethylhepta-1,5-dien-1-yl)-5-(4-(methoxycarbonyl)phenyl)pyrrolidine-3,3-dicarboxylate (*E*-10k)**



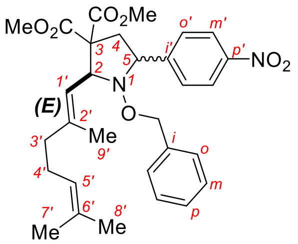

The title compound was prepared according to the procedure *A* from 2*E*-**2c**, **5k** (32 mg, 0.109 mmol, 1.4 equiv.), $Yb(NTf_2)_3$ (15.6 mg, 0.016 mmol, 20 mol.%), **L2** (3.7 mg, 0.018 mmol, 22 mol.%) at 40 °C, 24 h and 60 °C, 24 h as a mixture of diastereomers, *cis*/*trans* 6.5:1, in 29 mg yield (68%; dr of isolated fraction: 6.8:1). Eluent: petroleum ether/EtOAc 7:1. Colorless thick oil, $R_f$ = 0.50 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{32}H_{40}NO_7^+$ $[M+H]^+$ 550.2799, found: 550.2792. *E,cis*-**10k**, major: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 8.02 (d, $J$ = 8.3 Hz, 2H, 2×H(*m’*)), 7.61 (d, $J$ = 8.3 Hz, 2H, 2×H(*o’*)), 7.20–7.11 (m, 3H, 2×H(*m*), H(*p*)), 6.96–6.82 (m, 2H, 2×H(*o*)), 5.23 (dq, $^3J_{2,1'}$ = 9.8 Hz, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1’)), 5.16–5.03 (m, 1H, H(5’)), 4.67 (d, $^3J_{2,1'}$ = 9.8 Hz, 1H, H(2)), 4.52 and 4.19 (two doublets, $^2J_{HH}$ = 10.1 Hz, 2H, $CH_2$, Bn), 3.99 (dd, $^3J_{4a,5}$ = 11.4, $^3J_{4b,5}$ = 7.5 Hz, 1H, H(5)), 3.93 (s, 3H, *Ar*$CO_2Me$), 3.77 and 3.75 (both s, 2×3H, 2 $CO_2Me$), 2.77 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 11.4 Hz, 1H, $H_{syn}$(4a)), 2.52 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4b,5}$ = 7.5 Hz, 1H, $H_{anti}$(4b)), 2.20–1.99 (m, 4H, $CH_2$(3’), $CH_2$(4’)), 1.84 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9’)), 1.65 (br.s, 3H, $CH_3$(8’)), 1.60 (br.s, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.4 and 170.1 (2 COO), 167.0 (*Ar*COO), 145.9 (C(*i’*)), 142.2 (C(2’)), 136.8 (C(*i*)), 131.7 (C(6’)), 129.6 (C(*p’*)), 129.6 (2×CH(*m’*)), 128.6 (2×CH(*o*)), 128.2 (2×CH(*o’*)), 128.0 (2×CH(*m*)), 127.7 (CH(*p*)), 123.9 (CH(5’)), 121.0 (CH(1’)), 77.2 ($CH_2$, Bn), 69.1 (CH(2)), 69.0 (CH(5)), 59.7 (C(3)), 52.9 and 52.5 (2 $CO_2Me$), 52.0 (*Ar*$CO_2Me$), 40.0 ($CH_2$(3’)), 38.0 ($CH_2$(4)), 26.5 ($CH_2$(4’)), 25.6 ($CH_3$(8’)), 17.7 ($CH_3$(7’)), 17.0 ($CH_3$(9’)) ppm. *E,trans*-**10k**, minor: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.98 (d, $J$ = 8.3 Hz, 2H, 2×H(*m’*)), 7.44 (d, $J$ = 8.3 Hz, 2H, 2×H(*o’*)), 7.25–7.20 (m, 3H, 2×H(*m*), H(*p*)), 7.11–7.05 (m, 2H, 2×H(*o*)), 5.30–5.17 (m, 1H, H(1’)), 5.16–5.03 (m, 2H, H(2), H(5’)), 4.45 (dd, $^3J_{4b,5}$ = 9.3, $^3J_{4a,5}$ = 8.6 Hz, 1H, H(5)), 4.39 (two doublets, $^2J_{HH}$ = 11.6 Hz, 2H, $CH_2$, Bn), 3.92 (s, 3H, *Ar*$CO_2Me$), 3.75 and 3.61 (both s, 2×3H, 2 $CO_2Me$), 3.13 (dd, $^2J_{4a,4b}$ = 13.7, $^3J_{4a,5}$ = 8.6 Hz, 1H, $H_{syn}$(4a)), 2.37–2.29 (m, 1H, $H_{anti}$(4b)), 2.20–1.99 (m, 4H, $CH_2$(3’), $CH_2$(4’)), 1.68 (br.s, 3H, $CH_3$(8’)), 1.63 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9’)), 1.61 (m, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.2 and 169.4 (2 COO), 167.0 (*Ar*COO), 145.9 (C(*i’*)), 142.6 (C(2’)), 136.8 (C(*i*)), 131.8 (C(6’)), 129.5 (2×CH(*m’*)), 129.2 (C(*p’*)), 128.9 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.9 (2×CH(*o’*)), 127.6 (CH(*p*)), 123.9 (CH(5’)), 117.1 (CH(1’)), 75.6 ($CH_2$, Bn), 69.1 (CH(2)), 67.7 (CH(5)), 62.6 (C(3)), 52.9 and 52.5 (2 $CO_2Me$), 52.0 (*Ar*$CO_2Me$), 40.1 ($CH_2$(3’)), 36.4 ($CH_2$(4)), 26.7 ($CH_2$(4’)), 25.6 ($CH_3$(8’)), 17.7 ($CH_3$(7’)), 16.4 ($CH_3$(9’)) ppm.

**Dimethyl 1-(benzyloxy)-5-(4-cyanophenyl)-2-((*E*)-2,6-dimethylhepta-1,5-dien-1-yl)pyrrolidine-3,3-dicarboxylate (*E*-10l)**



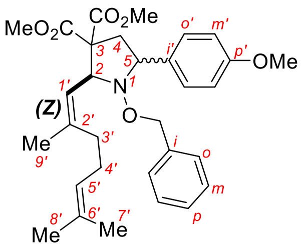

The title compound was prepared according to the procedure *A* from 2*E*-**2c**, **5l** (28 mg, 0.109 mmol, 1.4 equiv.), $Yb(NTf_2)_3$ (31.5 mg, 0.031 mmol, 40 mol.%), **L2** (7.0 mg, 0.035 mmol, 42 mol.%) at 60 °C, 30 h as a mixture of diastereomers, *cis*/*trans* 6.5:1, in 24 mg yield (60%; dr of isolated fraction: 7.5:1). Eluent: petroleum ether/EtOAc 7:1. Colorless thick oil, $R_f$ = 0.46 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{31}H_{37}N_2O_5^+$ $[M+H]^+$ 517.2697, found: 517.2688. *E,cis*-**10l**, major: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.62–7.57 (m, 4H, 2×H(*m’*), 2×H(*o’*)), 7.20–7.11 (m, 3H, 2×H(*m*), H(*p*)), 6.92–6.84 (m, 2H, 2×H(*o*)), 5.21 (dq, $^3J_{2,1'}$ = 9.8 Hz, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1’)), 5.16–5.06 (m, 1H, H(5’)), 4.68 (d, $^3J_{2,1'}$ = 9.8 Hz, 1H, H(2)), 4.53 and 4.21 (two doublets, $^2J_{HH}$ = 10.5 Hz, 2H, $CH_2$, Bn), 3.97 (dd, $^3J_{4a,5}$ = 11.2, $^3J_{4b,5}$ = 7.8 Hz, 1H, H(5)), 3.77 and 3.75 (both s, 2×3H, 2 $CO_2Me$), 2.70 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 11.2 Hz, 1H, $H_{syn}$(4a)), 2.51 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4b,5}$ = 7.8 Hz, 1H, $H_{anti}$(4b)), 2.18–2.02 (m, 4H, $CH_2$(3’), $CH_2$(4’)), 1.85 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9’)), 1.65 (br.s, 3H, $CH_3$(8’)), 1.60 (br.s, 3H, $CH_3$(7’)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.2 and 170.0 (2 COO), 146.3 (C(*i’*)), 142.4 (C(2’)), 136.8 (C(*i*)), 132.0 (2×CH(*m’*)), 131.8 (C(6’)), 128.9 (2×CH(*o’*)), 128.6 (2×CH(*o*)), 128.1 (2×CH(*m*)), 127.8 (CH(*p*)), 123.8 (CH(5’)), 120.8 (CH(1’)), 118.9 (C(*p’*)), 111.4 (CN), 77.1 ($CH_2$, Bn), 69.2 (CH(2)), 68.8 (CH(5)), 59.7 (C(3)), 52.9 and 52.5 (2 $CO_2Me$), 40.0 ($CH_2$(3')), 38.0 ($CH_2$(4)), 26.4 ($CH_2$(4')), 25.6 ($CH_3$(8')), 17.7 ($CH_3$(7')), 17.0 ($CH_3$(9')) ppm. *E,trans*-**10l**, minor: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.56 (d, $J$ = 8.3 Hz, 2H, 2×H($m'$)), 7.42 (d, $J$ = 8.3 Hz, 2H, 2×H($o'$)), 7.24–7.21 (m, 3H, 2×H($m$), H($p$)), 7.10–7.05 (m, 2H, 2×H($o$)), 5.26–5.17 (m, 1H, H(1')), 5.16–5.06 (m, 2H, H(2), H(5')), 4.41 (t, $^3J_{4a,5}$ = $^3J_{4b,5}$ = 8.7 Hz, 1H, H(5)), 4.40 (two doublets, $^2J_{HH}$ = 11.3 Hz, 2H, $CH_2$, Bn), 3.76 and 3.62 (both s, 2×3H, 2 $CO_2Me$), 3.13 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 8.7 Hz, 1H, $H_{syn}$(4a)), 2.32–2.25 (m, 1H, $H_{anti}$(4b)), 2.18–2.02 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.68 (br.s, 3H, $CH_3$(8')), 1.65 (m, 3H, $CH_3$(9')), 1.59 (m, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.2 and 169.4 (2 COO), 146.3 (C($i'$)), 143.0 (C(2')), 137.1 (C($i$)), 132.0 (2×CH($m'$)), 131.8 (C(6')), 128.9 (2×CH($o$)), 128.8 (2×CH($o'$)), 128.0 (2×CH($m$)), 127.7 (CH($p$)), 123.8 (CH(5')), 118.7 (C($p'$)), 117.2 (CH(1')), 110.9 (CN), 75.4 ($CH_2$, Bn), 68.0 (CH(2)), 67.1 (CH(5)), 62.3 (C(3)), 53.0 and 52.6 (2 $CO_2Me$), 40.0 ($CH_2$(3')), 36.3 ($CH_2$(4)), 26.6 ($CH_2$(4')), 25.6 ($CH_3$(8')), 17.7 ($CH_3$(7')), 16.5 ($CH_3$(9')) ppm.

**Dimethyl 1-(benzyloxy)-2-((*E*)-2,6-dimethylhepta-1,5-dien-1-yl)-5-(4-nitrophenyl)pyrrolidine-3,3-dicarboxylate (*E*-10m)**




The title compound was prepared according to the procedure *A* from 2*E*-**2c**, **5m** (30 mg, 0.109 mmol, 1.4 equiv.), $Yb(NTf_2)_3$ (31.5 mg, 0.031 mmol, 40 mol.%), **L2** (7.0 mg, 0.035 mmol, 42 mol.%) at 60 °C, 30 h as a mixture of diastereomers, *cis*/*trans* 6.3:1, in 39 mg yield (94%; dr of isolated fraction: 6.3:1). Eluent: petroleum ether/EtOAc 8:1. Yellowish thick oil, $R_f$ = 0.55 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{30}H_{37}N_2O_7^+$ [M+H]$^+$ 537.2595, found: 537.2607. *E,cis*-**10m**, major: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 8.14 (d, $J$ = 8.8 Hz, 2H, 2×H($m'$)), 7.64 (d, $J$ = 8.8 Hz, 2H, 2×H($o'$)), 7.20–7.09 (m, 3H, 2×H($m$), H($p$)), 6.94–6.84 (m, 2H, 2×H($o$)), 5.23 (dq, $^3J_{2,1'}$ = 9.8 Hz, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 5.18–5.04 (m, 1H, H(5')), 4.70 (d, $^3J_{2,1'}$ = 9.8 Hz, 1H, H(2)), 4.55 and 4.24 (two doublets, $^2J_{HH}$ = 10.5 Hz, 2H, $CH_2$, Bn), 4.03 (dd, $^3J_{4a,5}$ = 11.1, $^3J_{4b,5}$ = 7.8 Hz, 1H, H(5)), 3.78 and 3.76 (both s, 2×3H, 2 $CO_2Me$), 2.72 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 11.1 Hz, 1H, $H_{syn}$(4a)), 2.54 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4b,5}$ = 7.8 Hz, 1H, $H_{anti}$(4b)), 2.20–2.00 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.86 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.65 (br.s, 3H, $CH_3$(8')), 1.61 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.1 and 170.0 (2 COO), 148.3 (C($i'$)), 147.5 (C($p'$)), 142.5 (C(2')), 136.8 (C($i$)), 131.8 (C(6')), 128.9 (2×CH($o'$)), 128.6 (2×CH($o$)), 128.0 (2×CH($m$)), 127.8 (CH($p$)), 123.8 (CH(5')), 123.4 (2×CH($m'$)), 120.8 (CH(1')), 77.1 ($CH_2$, Bn), 69.3 (CH(5)), 68.5 (CH(2)), 59.7 (C(3)), 53.0 and 52.5 (2 $CO_2Me$), 40.0 ($CH_2$(3')), 38.1 ($CH_2$(4)), 26.4 ($CH_2$(4')), 25.6 ($CH_3$(8')), 17.7 ($CH_3$(7')), 17.0 ($CH_3$(9')) ppm. *E,trans*-**10m**, minor: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 8.11 (d, $J$ = 8.8 Hz, 2H, 2×H($m'$)), 7.46 (d, $J$ = 8.8 Hz, 2H, 2×H($o'$)), 7.23–7.21 (m, 3H, 2×H($m$), H($p$)), 7.10–7.05 (m, 2H, 2×H($o$)), 5.30–5.18 (m, 1H, H(1')), 5.18–5.04 (m, 1H, H(5')), 5.16 (d, $^3J_{2,1'}$ = 10.4 Hz, 1H, H(2)), 4.46 (t, $^3J_{4a,5}$ = $^3J_{4b,5}$ = 8.8 Hz, 1H, H(5)), 4.41 (two doublets, $^2J_{HH}$ = 11.3 Hz, 2H, $CH_2$, Bn), 3.77 and 3.63 (both s, 2×3H, 2 $CO_2Me$), 3.18 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 8.8 Hz, 1H, $H_{syn}$(4a)), 2.35–2.26 (m, 1H, $H_{anti}$(4b)), 2.20–2.00 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.68 (br.s, 3H, $CH_3$(8')), 1.66 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.61 (m, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.0 and 169.1 (2 COO), 148.4 (C($i'$)), 147.5 (C($p'$)), 143.1 (C(2')), 137.1 (C($i$)), 131.8 (C(6')), 129.0 (2×CH($o'$)), 128.6 (2×CH($o$)), 128.0 (2×CH($m$)), 127.8 (CH($p$)), 123.8 (CH(5')), 123.4 (2×CH($m'$)), 117.1 (CH(1')), 75.4 ($CH_2$, Bn), 68.9 (CH(2)), 66.9 (CH(5)), 62.3 (C(3)), 53.0 and 52.6 (2 $CO_2Me$), 40.1 ($CH_2$(3')), 36.3 ($CH_2$(4)), 26.6 ($CH_2$(4')), 25.6 ($CH_3$(8')), 17.7 ($CH_3$(7')), 16.5 ($CH_3$(9')) ppm.

**Dimethyl 1-(benzyloxy)-2-((*Z*)-2,6-dimethylhepta-1,5-dien-1-yl)-5-(4-methoxyphenyl)pyrrolidine-3,3-dicarboxylate (*Z*-10a)**




The title compound was prepared according to the procedure *A* from 2*Z*-**2c**, **5a** (42 mg, 0.156 mmol, 2 equiv.), $Yb(NTf_2)_3$ (3.9 mg, 0.004 mmol, 5 mol.%), **L2** (1.0 mg, 0.005 mmol, 6 mol.%) at 20 °C, 48 h as a mixture of diastereomers, *cis*/*trans* 6:1, in 40 mg yield (95%; dr of isolated fraction: 7.7:1), or procedure *B* in 1.24 g yield as a mixture of diastereomers, *cis*/*trans* 6:1 (total yield 84%; 720 mg of *Z,cis*-**10a**, *cis*/*trans* >30:1, was partially isolated). Eluent: petroleum ether/EtOAc 10:1. Colorless thick oil, $R_f$ = 0.55 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{31}H_{40}NO_6^+$ [M+H]$^+$ 522.2850, found: 522.2843.

NMR spectra were recorded at 300 and 600 MHz. *Z,cis*-**10a**, major: $^{1}$H NMR (600.1 MHz, $CDCl_3$): δ 7.45 (d, $J$ = 8.7 Hz, 2H, 2×H(*o'*)), 7.19–7.12 (m, 3H, 2×H(*m*), H(*p*)), 6.98–6.90 (m, 2H, 2×H(*o*)), 6.88 (d, $J$ = 8.7 Hz, 2H, 2×H(*m'*)), 5.18–5.06 (m, 2H, H(1'), H(5')), 4.61 (d, $^{3}J_{2,1'}$ = 9.9 Hz, 1H, H(2)), 4.41 and 4.17 (two doublets, $^{2}J_{HH}$ = 10.2 Hz, 2H, $CH_2$, Bn), 3.86 (dd, $^{3}J_{4a,5}$ = 11.6, $^{3}J_{4b,5}$ = 7.2 Hz, 1H, H(5)), 3.82 (s, 3H, OMe), 3.74 and 3.72 (both s, 2×3H, 2 $CO_2Me$), 2.79 (dd, $^{2}J_{4a,4b}$ = 13.7, $^{3}J_{4a,5}$ = 11.6 Hz, 1H, $H_{syn}$(4a)), 2.43 (dd, $^{2}J_{4a,4b}$ = 13.7, $^{3}J_{4b,5}$ = 7.2 Hz, 1H, $H_{anti}$(4b)), 2.35–1.98 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.76 (d, $^{4}J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.65 (br.s, 3H, $CH_3$(8')), 1.57 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): δ 171.5 and 170.3 (2 COO), 159.2 (C(*p'*)), 141.8 (C(2')), 137.2 (C(*i*)), 132.4 (C(*i'*)), 131.3 (C(6')), 129.4 (2×CH(*o'*)), 128.9 (2×CH(*o*)), 127.9 (2×CH(*m*)), 127.5 (CH(*p*)), 124.5 (CH(5')), 122.2 (CH(1')), 113.6 (2×CH(*m'*)), 77.1 ($CH_2$, Bn), 68.5 (CH(5)), 68.3 (CH(2)), 59.6 (C(3)), 55.2 (OMe), 52.8 and 52.3 (2 $CO_2Me$), 38.0 ($CH_2$(4)), 32.4 ($CH_2$(3')), 26.7 ($CH_2$(4')), 25.6 ($CH_3$(8')), 23.9 ($CH_3$(9')), 17.6 ($CH_3$(7')) ppm. *Z,trans*-**10a**, minor: $^{1}$H NMR (600.1 MHz, $CDCl_3$): δ 7.30 (d, $J$ = 8.7 Hz, 2H, 2×H(*o'*)), 7.23–7.18 (m, 3H, 2×H(*m*), H(*p*)), 7.09–7.04 (m, 2H, 2×H(*o*)), 6.84 (d, $J$ = 8.7 Hz, 2H, 2×H(*m'*)), 5.35–5.00 (m, 3H, H(2), H(1'), H(5')), 4.38–4.30 (m, 1H, H(5)), 4.36 and 4.34 (two doublets, $^{2}J_{HH}$ = 11.3 Hz, 2H, $CH_2$, Bn), 3.81 (s, 3H, OMe), 3.74 and 3.61 (both s, 2×3H, 2 $CO_2Me$), 3.05 (dd, $^{2}J_{4a,4b}$ = 13.7, $^{3}J_{4a,5}$ = 8.2 Hz, 1H, $H_{syn}$(4a)), 2.49–2.35 (m, 1H, $H_{anti}$(4b)), 2.35–1.98 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.76 (br.s, 3H, $CH_3$(8')), 1.70 (m, 3H, $CH_3$(9')), 1.63 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): δ 171.4 and 169.9 (2 COO), 159.0 (C(*p'*)), 142.4 (C(2')), 137.4 (C(*i*)), 137.5 (C(*i'*)), 131.7 (C(6')), 129.4 (2×CH(*o'*)), 128.8 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.5 (CH(*p*)), 124.1 (CH(5')), 118.6 (CH(1')), 113.5 (2×CH(*m'*)), 75.6 ($CH_2$, Bn), 68.3 (CH(2)), 67.4 (CH(5)), 58.6 (C(3)), 55.2 (OMe), 52.8 and 52.4 (2 $CO_2Me$), 36.7 ($CH_2$(4)), 32.3 ($CH_2$(3')), 26.6 ($CH_2$(4')), 25.7 ($CH_3$(8')), 23.8 ($CH_3$(9')), 17.6 ($CH_3$(7')) ppm.

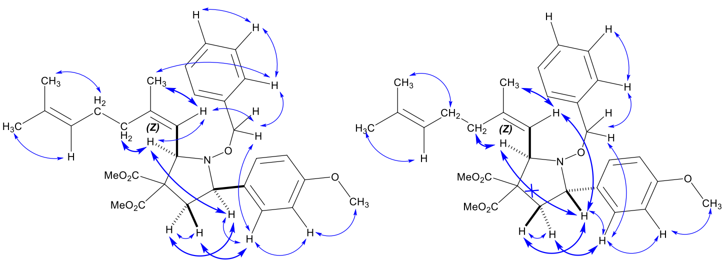
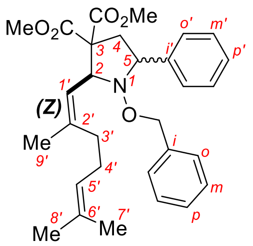


**Figure S6.** Key nOe interactions for the isomers of *Z*-**10a** from the NOESY data

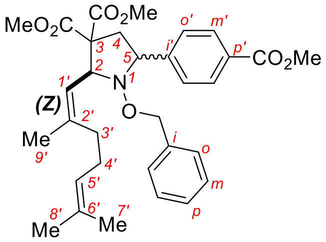
**Dimethyl 1-(benzyloxy)-2-((*Z*)-2,6-dimethylhepta-1,5-dien-1-yl)-5-phenylpyrrolidine-3,3-dicarboxylate (*Z*-10d)**



The title compound was prepared according to the procedure *A* from 2*Z*-**2c**, **5d** (29 mg, 0.125 mmol, 1.6 equiv.), $Yb(NTf_2)_3$ (15.6 mg, 0.016 mmol, 20 mol.%), **L2** (3.7 mg, 0.018 mmol, 22 mol.%) at 40 °C, 24 h as a mixture of diastereomers, *cis*/*trans* 5.9:1, in 34 mg yield (89%; dr of isolated fraction: 6.2:1). Eluent: petroleum ether/EtOAc 12:1. Colorless thick oil, $R_f$ = 0.59 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m*/*z*: calcd for $C_{30}H_{38}NO_5^+$ $[M+H]^+$ 492.2744, found: 492.2738. *Z,cis*-**10d**, major: $^{1}$H NMR (300.1 MHz, $CDCl_3$): δ 7.59–7.50 (m, 2H, 2×H(*o'*)), 7.41–7.26 (m, 3H, 2×H(*m'*), H(*p'*)), 7.18–7.11 (m, 3H, 2×H(*m*), H(*p*)), 6.95–6.85 (m, 2H, 2×H(*o*)), 5.19–5.09 (m, 2H, H(1'), H(5')), 4.63 (d, $^{3}J_{2,1'}$ = 9.9 Hz, 1H, H(2)), 4.43 and 4.18 (two doublets, $^{2}J_{HH}$ = 10.2 Hz, 2H, $CH_2$, Bn), 3.91 (dd, $^{3}J_{4a,5}$ = 11.6, $^{3}J_{4b,5}$ = 7.3 Hz, 1H, H(5)), 3.75 and 3.73 (both s, 2×3H, 2 $CO_2Me$), 2.81 (dd, $^{2}J_{4a,4b}$ = 13.7, $^{3}J_{4a,5}$ = 11.6 Hz, 1H, $H_{syn}$(4a)), 2.43 (dd, $^{2}J_{4a,4b}$ = 13.7, $^{3}J_{4b,5}$ = 7.3 Hz, 1H, $H_{anti}$(4b)), 2.35–1.98 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.76 (d, $^{4}J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.65 (br.s, 3H, $CH_3$(8')), 1.57 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.5 and 170.2 (2 COO), 141.9 (C(2')), 140.4 (C(*i'*)), 137.1 (C(*i*)), 131.4 (C(6')), 128.9 (2×CH(*o*)), 128.3 (2×CH(*o'*)), 128.2 (2×CH(*m'*)), 127.9 (2×CH(*m*)), 127.7 (CH(*p'*)), 127.6 (CH(*p*)), 124.4 (CH(5')), 122.1 (CH(1')), 77.2 ($CH_2$, Bn), 69.2 (CH(5)), 68.4 (CH(2)), 59.7 (C(3)), 52.8 and 52.4 (2 $CO_2Me$), 38.1 ($CH_2$(4)), 32.4 ($CH_2$(3')), 26.7 ($CH_2$(4')), 25.6 ($CH_3$(8')), 23.9 ($CH_3$(9')), 17.6 ($CH_3$(7')) ppm. *Z,trans*-**10d**, minor: $^{1}$H NMR (300.1 MHz, $CDCl_3$): δ 7.41–7.26 (m, 5H, 2×H(*o'*), 2×H(*m'*), H(*p'*)), 7.22–7.18 (m, 3H, 2×H(*m*), H(*p*)), 7.07–7.01 (m, 2H, 2×H(*o*)), 5.28–5.19 (m, 2H, H(2), H(1')), 5.19–5.09 (m, 1H, H(5')), 4.46–4.32 (m, 1H, H(5)), 4.37 (two doublets,

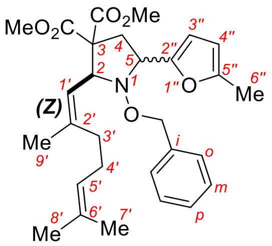
$^{2}J_{HH}$ = 11.4 Hz, 2H, $CH_2$, Bn), 3.74 and 3.61 (both s, 2×3H, 2 $CO_2Me$), 3.10 (dd, $^{2}J_{4a,4b}$ = 13.7, $^{3}J_{4a,5}$ = 8.3 Hz, 1H, $H_{syn}$(4a)), 2.52–2.37 (m, 1H, $H_{anti}$(4b)), 2.35–1.98 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.70 (br.s, 3H, $CH_3$(8')), 1.76 (m, 3H, $CH_3$(9')), 1.63 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.3 and 169.8 (2 COO), 142.1 (C(2')), 137.3 (C(*i*)), 140.5 (C(*i'*)), 131.7 (C(6')), 128.8 (2×CH(*o*)), 128.3 and 128.1 (2×CH(*o'*) and 2×CH(*m'*)), 128.0 (2×CH(*m*)), 127.4 and 127.5 (CH(*p*) and CH(*p'*)), 124.1 (CH(5')), 118.4 (CH(1')), 75.6 ($CH_2$, Bn), 68.0 (CH(2) and CH(5)), 59.7 (C(3)), 52.8 and 52.5 (2 $CO_2Me$), 36.6 ($CH_2$(4)), 32.3 ($CH_2$(3')), 26.6 ($CH_2$(4')), 25.7 ($CH_3$(8')), 23.9 ($CH_3$(9')), 17.4 ($CH_3$(7')) ppm.

**Dimethyl 1-(benzyloxy)-2-((*Z*)-2,6-dimethylhepta-1,5-dien-1-yl)-5-(4-(methoxycarbonyl)phenyl)pyrrolidine-3,3-dicarboxylate (*Z*-10k)**



The title compound was prepared according to the procedure *A* from 2*Z*-**2c**, **5k** (36 mg, 0.125 mmol, 1.6 equiv.), Yb($NTf_2$)$_3$ (23.4 mg, 0.024 mmol, 30 mol.%), **L2** (5.9 mg, 0.029 mmol, 32 mol.%) at 60 °C, 24 h as a mixture of diastereomers, *cis*/*trans* 5.9:1, in 30 mg yield (70%; dr of isolated fraction: 6.2:1). Eluent: petroleum ether/EtOAc 7:1. Colorless thick oil, $R_f$ = 0.47 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{32}H_{40}NO_7^+$ $[M+H]^+$ 550.2799, found: 550.2792. *Z,cis*-**10k**, major: $^{1}$H NMR (300.1 MHz, $CDCl_3$): δ 8.01 (d, *J* = 8.3 Hz, 2H, 2×H(*m'*)), 7.60 (d, *J* = 8.3 Hz, 2H, 2×H(*o'*)), 7.18–7.09 (m, 3H, 2×H(*m*), H(*p*)), 6.94–6.85 (m, 2H, 2×H(*o*)), 5.20–5.08 (m, 2H, H(1'), H(5')), 4.66 (d, $^{3}J_{2,1'}$ = 9.9 Hz, 1H, H(2)), 4.46 and 4.20 (two doublets, $^{2}J_{HH}$ = 10.3 Hz, 2H, $CH_2$, Bn), 3.98 (dd, $^{3}J_{4a,5}$ = 11.5, $^{3}J_{4b,5}$ = 7.4 Hz, 1H, H(5)), 3.93 (s, 3H, *Ar*$CO_2Me$), 3.76 and 3.73 (both s, 2×3H, 2 $CO_2Me$), 2.77 (dd, $^{2}J_{4a,4b}$ = 13.8, $^{3}J_{4a,5}$ = 11.5 Hz, 1H, $H_{syn}$(4a)), 2.49 (dd, $^{2}J_{4a,4b}$ = 13.8, $^{3}J_{4b,5}$ = 7.4 Hz, 1H, $H_{anti}$(4b)), 2.35–1.98 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.78 (d, $^{4}J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.66 (br.s, 3H, $CH_3$(8')), 1.57 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.3 and 170.0 (2 COO), 167.0 (*Ar*COO), 145.9 (C(*i'*)), 142.2 (C(2')), 136.8 (C(*i*)), 131.4 (C(6')), 129.6 (C(*p'*)), 129.6 (2×CH(*m'*)), 128.8 (2×CH(*o*)), 128.2 (2×CH(*o'*)), 127.9 (2×CH(*m*)), 127.6 (CH(*p*)), 124.3 (CH(5')), 121.8 (CH(1')), 77.2 ($CH_2$, Bn), 68.9 (CH(5)), 68.6 (CH(2)), 59.7 (C(3)), 52.9 and 52.4 (2 $CO_2Me$), 52.0 (*Ar*$CO_2Me$), 38.1 ($CH_2$(4)), 32.4 ($CH_2$(3')), 26.7 ($CH_2$(4')), 25.6 ($CH_3$(8')), 23.9 ($CH_3$(9')), 17.6 ($CH_3$(7')) ppm. *Z,trans*-**10k**, minor: $^{1}$H NMR (300.1 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.3 Hz, 2H, 2×H(*m'*)), 7.43 (d, *J* = 8.3 Hz, 2H, 2×H(*o'*)), 7.23–7.17 (m, 3H, 2×H(*m*), H(*p*)), 7.07–7.00 (m, 2H, 2×H(*o*)), 5.24–5.20 (m, 2H, H(2), H(1')), 5.20–5.08 (m, 1H, H(5')), 4.49–4.41 (m, 1H, H(5)), 4.38 (s, 2H, $CH_2$, Bn), 3.92 (s, 3H, *Ar*$CO_2Me$), 3.75 and 3.62 (both s, 2×3H, 2 $CO_2Me$), 3.13 (dd, $^{2}J_{4a,4b}$ = 13.7, $^{3}J_{4a,5}$ = 8.4 Hz, 1H, $H_{syn}$(4a)), 2.44–2.35 (m, 1H, $H_{anti}$(4b)), 2.35–1.98 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.82–1.73 (m, 3H, $CH_3$(9')), 1.70 (br.s, 3H, $CH_3$(8')), 1.64 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.1 and 169.7 (2 COO), 166.5 (*Ar*COO), 145.8 (C(*i'*)), 142.9 (C(2')), 137.0 (C(*i*)), 131.8 (C(6')), 129.4 (2×CH(*m'*)), 129.2 (C(*p'*)), 128.9 (2×CH(*o*)), 128.0 (2×CH(*o'*)), 128.0 (2×CH(*m*)), 127.8 (CH(*p*)), 124.0 (CH(5')), 118.1 (CH(1')), 75.5 ($CH_2$, Bn), 67.5 (CH(5)), 66.6 (CH(2)), 59.7 (C(3)), 52.9 and 52.6 (2 $CO_2Me$), 52.0 (*Ar*$CO_2Me$), 36.5 ($CH_2$(4)), 32.3 ($CH_2$(3')), 26.6 ($CH_2$(4')), 25.7 ($CH_3$(8')), 23.8 ($CH_3$(9')), 17.6 ($CH_3$(7')) ppm.

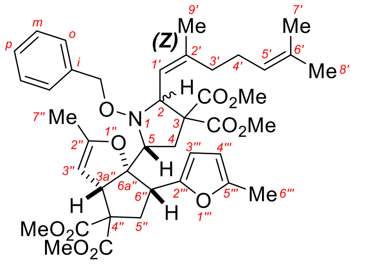
**Dimethyl 1-(benzyloxy)-2-((*Z*)-2,6-dimethylhepta-1,5-dien-1-yl)-5-(5-methylfuran-2-yl)pyrrolidine-3,3-dicarboxylate (*Z*-10e)**



The title compound was prepared according to the procedure *A* from 2*Z*-**2c**, **5e** (56 mg, 0.234 mmol, 3 equiv.), Yb($NTf_2$)$_3$ (7.8 mg, 0.008 mmol, 10 mol.%), **L2** (1.8 mg, 0.009 mmol, 11 mol.%) at -15 °C, 7 d as a mixture of diastereomers, *cis*/*trans* 2.9:1, in 12 mg yield (31%), or procedure *C* as a mixture of diastereomers, *cis*/*trans* 2.9:1, in 20 mg yield (52%; dr of isolated fraction: 3.3:1). Eluent: petroleum ether/EtOAc 10:1. Colorless thick oil, $R_f$ = 0.58 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{29}H_{38}NO_6^+$ $[M+H]^+$ 496.2694, found: 496.2684. *Z,cis*-**10e**, major: $^{1}$H NMR (300.1 MHz, $CDCl_3$): δ 7.32–7.18 (m, 3H, 2×H(*m*), H(*p*)), 7.18–7.04 (m, 2H, 2×H(*o*)), 6.24 (d, $^{3}J_{3'',4''}$ = 3.0 Hz, 1H, H(3'')), 5.93 (dq, $^{3}J_{3'',4''}$ = 3.0 Hz, $^{4}J_{4'',6''}$ = 1.0 Hz, 1H, H(4'')), 5.17–5.10 (m, 2H, H(1'), H(5')), 4.61 (d, $^{3}J_{2,1'}$ = 10.0 Hz, 1H, H(2)), 4.47 and 4.33 (two doublets, $^{2}J_{HH}$ = 10.0 Hz, 2H, $CH_2$, Bn), 3.94 (dd, $^{3}J_{4a,5}$ = 12.0, $^{3}J_{4b,5}$ = 6.7 Hz, 1H, H(5)), 3.74 and 3.70 (both s, 2×3H, 2 $CO_2Me$), 3.06 (dd, $^{2}J_{4a,4b}$ = 13.6, $^{3}J_{4a,5}$ = 12.1 Hz, 1H, $H_{syn}$(4a)), 2.49 (dd,

$^{2}J_{4a,4b}$ = 13.6, $^{3}J_{4b,5}$ = 6.7 Hz, 1H, $H_{anti}$(4b)), 2.31 (d, $^{4}J_{4'',6''}$ = 1.0 Hz, 3H, $CH_3$(6'')), 2.24–1.94 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.74 (d, $^{4}J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.65 (br.s, 3H, $CH_3$(8')), 1.56 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.4 and 169.8 (2 COO), 151.9 (C(5'')), 150.6 (C(2'')), 141.9 (C(2')), 137.1 (C(*i*)), 131.4 (C(6')), 129.0 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.7 (CH(*p*)), 124.4 (CH(5')), 121.8 (CH(1')), 109.1 (CH(3'')), 106.2 (CH(4'')), 77.1 ($CH_2$, Bn), 68.2 (CH(2)), 62.2 (CH(5)), 59.6 (C(3)), 52.9 and 52.4 (2 $CO_2Me$), 34.2 ($CH_2$(4)), 32.4 ($CH_2$(3')), 26.7 ($CH_2$(4')), 25.6 ($CH_3$(8')), 23.8 ($CH_3$(9')), 17.6 ($CH_3$(7')), 13.7 ($CH_3$(6'')) ppm. *Z,trans*-**10e**, minor: $^{1}$H NMR (300.1 MHz, $CDCl_3$): δ 7.32–7.18 (m, 3H, 2×H(*m*), H(*p*)), 7.18–7.04 (m, 2H, 2×H(*o*)), 6.15 (d, $^{3}J_{3'',4''}$ = 3.0 Hz, 1H, H(3'')), 5.91 (dq, $^{3}J_{3'',4''}$ = 3.0 Hz, $^{4}J_{4'',6''}$ = 1.0 Hz, 1H, H(4'')), 5.29–5.17 (d, $^{3}J_{2,1'}$ = 10.7 Hz, 1H, H(2)), 5.17–5.10 (m, 1H, H(5')), 5.08 (d, $^{3}J_{2,1'}$ = 10.7 Hz, 1H, H(1')), 4.43 (dd, $^{3}J_{4b,5}$ = 9.8, $^{3}J_{4a,5}$ = 7.6 Hz, 1H, H(5)), 4.49 and 4.40 (two doublets, $^{2}J_{HH}$ = 11.2 Hz, 2H, $CH_2$, Bn), 3.73 and 3.61 (both s, 2×3H, 2 $CO_2Me$), 2.99 (dd, $^{2}J_{4a,4b}$ = 13.4, $^{3}J_{4a,5}$ = 7.6 Hz, 1H, $H_{syn}$(4a)), 2.64 (dd, $^{2}J_{4a,4b}$ = 13.4, $^{3}J_{4b,5}$ = 9.8 Hz, 1H, $H_{anti}$(4b)), 2.26 (d, $^{4}J_{4'',6''}$ = 1.0 Hz, 3H, $CH_3$(6'')), 2.24–1.94 (m, 4H, $CH_2$(3'), $CH_2$(4')), 1.72 (d, $^{4}J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.69 (br.s, 3H, $CH_3$(8')), 1.62 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.2 and 170.1 (2 COO), 151.5 (C(5'')), 150.6 (C(2'')), 141.9 (C(2')), 137.6 (C(*i*)), 131.7 (C(6')), 128.6 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.5 (CH(*p*)), 124.1 (CH(5')), 119.0 (CH(1')), 109.1 (CH(3'')), 106.1 (CH(4'')), 75.5 ($CH_2$, Bn), 69.2 (CH(2)), 62.6 (CH(5)), 59.2 (C(3)), 52.8 and 52.4 (2 $CO_2Me$), 34.9 ($CH_2$(4)), 32.3 ($CH_2$(3')), 26.5 ($CH_2$(4')), 25.7 ($CH_3$(8')), 23.8 ($CH_3$(9')), 17.6 ($CH_3$(7')), 13.6 ($CH_3$(6'')) ppm.

**Dimethyl 1-(benzyloxy)-5-((3a*RS*,6*RS*,6a*RS*)-4,4-bis(methoxycarbonyl)-2-methyl-6-(5-methylfuran-2-yl)-3a,4,5,6-tetrahydro-6a*H*-cyclopenta[*b*]furan-6a-yl)-2-((*Z*)-2,6-dimethylhepta-1,5-dien-1-yl)pyrrolidine-3,3-dicarboxylate (11)**



The title compound was prepared according to the procedure *A* from 2*Z*-**2c**, **5e** (56 mg, 0.234 mmol, 3 equiv.), Yb($NTf_2$)$_3$ (7.8 mg, 0.008 mmol, 10 mol.%), **L2** (1.8 mg, 0.009 mmol, 11 mol.%) at -15 °C, 7 d as a mixture of diastereomers, (2*RS*,5*SR*)/(2*RS*,5*RS*) 1:1, in 16 mg yield (28%; 5 mg of (2*RS*,5*SR*)-**11** and 11 mg of **11** as a mixture of diastereomers, (2*RS*,5*RS*)/(2*RS*,5*SR*) 2.8:1, were partially isolated), or procedure *C* as a mixture of diastereomers, (2*RS*,5*SR*)/(2*RS*,5*RS*) 1:1, in 5.5 mg yield (10%). Eluent: petroleum ether/EtOAc 4:1. Colorless solid, mp 60–62 °C. HRMS (ESI) *m/z*: calcd for $C_{41}H_{52}NO_{11}^{+}$ [M+H]$^{+}$ 734.3535, found: 734.3527. (2*RS*,5*SR*)-**11**: $R_f$ = 0.63 (petroleum ether/EtOAc 3:1). $^{1}$H NMR (300.1 MHz, $CDCl_3$): δ 7.38–7.18 (m, 5H, Bn), 5.98 (d, $^{3}J_{3''',4'''}$ = 3.0 Hz, 1H, H(3''')), 5.86 (dq, $^{3}J_{3''',4'''}$ = 3.0, $^{4}J_{4''',6'''}$ = 1.0 Hz, 1H, H(4''')), 5.38 (d, $^{3}J_{2,1'}$ = 9.8 Hz, 1H, H(1')), 5.17–5.07 (m, 1H, H(5')), 4.79 and 4.60 (two doublets, $^{2}J_{HH}$ = 10.4 Hz, 2H, $CH_2$, Bn), 4.51 (d, $^{3}J_{2,1'}$ = 9.8 Hz, 1H, H(2)), 4.45–4.40 (m, 1H, H(3a'')), 4.24 (dq, $^{3}J_{3'',3a''}$ = 2.6, $^{4}J_{3'',1'}$ = 1.2 Hz, 1H, H(3'')), 3.97 (dd, $^{3}J_{4a,5}$ = 9.1, $^{3}J_{4b,5}$ = 6.3 Hz, 1H, H(5)), 3.74, 3.73, 3.60 and 3.53 (four s, 4×3H, 4 $CO_2Me$), 3.20 (dd, $^{3}J_{5''b,6''}$ = 14.3, $^{3}J_{5''a,6''}$ = 6.0 Hz, 1H, H(6'')), 2.94 (dd, $^{2}J_{4a,4b}$ = 13.6, $^{2}J_{4a,5}$ = 9.1 Hz, 1H, $H_{syn}$(4a)), 2.68 (dd, $^{3}J_{5''b,6''}$ = 14.3, $^{2}J_{5''a,5''b}$ = 13.3 Hz, 1H, $H_{anti}$(5''b)), 2.36 (ddd, $^{2}J_{5''a,5''b}$ = 13.3, $^{3}J_{5''a,6''}$ = 6.0, $^{3}J_{5''a,3a''}$ = 1.3 Hz, 1H, $H_{syn}$(5''a)), 2.23 (d, $^{4}J_{4''',6'''}$ = 1.0 Hz, 3H, $CH_3$(6''')), 2.25–2.13 (m, 1H, H(3'a)), 2.11–2.00 (m, 3H, H(3'b), $CH_2$(4')), 2.04 (dd, $^{2}J_{4a,4b}$ = 13.6, $^{3}J_{4b,5}$ = 6.3 Hz, 1H, $H_{anti}$(4b)), 1.74 (d, $^{4}J_{1',9'}$ = 1.5 Hz, 3H, $CH_3$(9')), 1.73 (br.s, 3H, $CH_3$(7'')), 1.67 (br.s, 3H, $CH_3$(8')), 1.60 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.6, 171.0, 170.2 and 169.9 (4 COO), 157.6 (C(2'')), 150.4 and 150.3 (C(2''') and C(5''')), 141.3 (C(2')), 137.6 (C(*i*)), 131.2 (C(6')), 128.4 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.3 (CH(*p*)), 124.6 (CH(5')), 118.9 (CH(1')), 108.6 (CH(3''')), 106.2 (CH(4''')), 95.7 (C(6a'')), 94.6 (CH(3'')), 75.1 ($CH_2$, Bn), 73.8 (CH(5)), 69.0 (CH(2)), 63.6 and 63.3 (C(3) and C(4'')), 56.8 (CH(3a'')), 52.8, 52.3, 52.3 and 52.2 (4 $CO_2Me$), 45.9 (CH(6'')), 36.7 ($CH_2$(5'')), 32.8 ($CH_2$(4)), 32.2 ($CH_2$(3')), 26.7 ($CH_2$(4')), 25.6 ($CH_3$(8')), 23.8 ($CH_3$(9')), 17.7 ($CH_3$(7')), 13.6 ($CH_3$(7'')), 13.5 ($CH_3$(6''')) ppm. (2*RS*,5*RS*)-**11**: $R_f$ = 0.57 (petroleum ether/EtOAc 3:1). $^{1}$H NMR (300.1 MHz, $CDCl_3$): δ 7.34–7.17 (m, 5H, Bn), 5.95 (d, $^{3}J_{3''',4'''}$ = 3.0 Hz, 1H, H(3''')), 5.84–5.80 (dq, $^{3}J_{3''',4'''}$ = 3.0, $^{4}J_{4''',6'''}$ = 1.0 Hz, 1H, H(4''')), 5.28 (d, $^{3}J_{2,1'}$ = 10.5 Hz, 1H, H(1')), 5.17–5.05 (m, 1H, H(5')), 4.92 (d, $^{3}J_{2,1'}$ = 10.5 Hz, 1H, H(2)), 4.62 (two doublets, $^{2}J_{HH}$ = 10.2 Hz, 2H, $CH_2$, Bn), 4.38–4.34 (m, 1H, H(3'')), 4.35–4.31 (m, 1H, H(3a'')), 3.74, 3.73, 3.70 and 3.60 (four s, 4×3H, 4 $CO_2Me$), 3.49 (dd, $^{3}J_{4b,5}$ = 11.2, $^{3}J_{4a,5}$ = 7.8 Hz, 1H, H(5)), 3.39 (dd, $^{3}J_{5''b,6''}$ = 14.2, $^{3}J_{5''a,6''}$ = 5.9 Hz, 1H, H(6'')), 2.69 (dd, $^{3}J_{5''b,6''}$ = 14.2, $^{2}J_{5''a,5''b}$ = 13.0 Hz, 1H, $H_{anti}$(5''b)), 2.51 (ddd, $^{2}J_{5''a,5''b}$ = 13.0, $^{3}J_{5''a,6''}$ = 5.9,

$^3J_{5''a,3a''}$ = 1.0 Hz, 1H, H$_{syn}$(5''a)), 2.50 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4b,5}$ = 11.2, 1H, H$_{anti}$(4b)), 2.40 (dd, $^2J_{4a,4b}$ = 13.8, $^3J_{4a,5}$ = 7.8 Hz, 1H, H$_{syn}$(4a)), 2.21 (d, $^4J_{4''',6'''}$ = 1.0 Hz, 3H, CH$_3$(6''')), 2.24–2.14 (m, 1H, H(3'a)), 2.12–1.96 (m, 3H, H(3'b), CH$_2$(4')), 1.76 (br.s, 3H, CH$_3$(7'')), 1.74 (br.s, 3H, CH$_3$(9')), 1.64 (br.s, 3H, CH$_3$(8')), 1.57 (br.s, 3H, CH$_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, CDCl$_3$): δ 171.1, 170.9, 169.7 and 169.1 (4 COO), 157.8 (C(2'')), 150.4 and 150.2 (C(2''') and C(5''')), 138.8 (C(2')), 137.0 (C(*i*)), 131.7 (C(6')), 128.6 (2×CH(*o*)), 128.1 (2×CH(*m*)), 127.5 (CH(*p*)), 124.1 (CH(5')), 123.3 (CH(1')), 108.6 (CH(3''')), 106.2 (CH(4''')), 96.2 (C(6a'')), 94.7 (CH(3'')), 75.4 (CH$_2$, Bn), 70.6 (CH(2)), 68.8 (CH(5)), 64.2 and 61.6 (C(3) and C(4'')), 55.1 (CH(3a'')), 52.9, 52.7, 52.4 and 52.2 (4 CO$_2$Me), 44.1 (CH(6'')), 35.4 (CH$_2$(5'')), 32.2 (CH$_2$(3')), 31.8 (CH$_2$(4)), 26.4 (CH$_2$(4')), 25.6 (CH$_3$(8')), 23.5 (CH$_3$(9')), 17.6 (CH$_3$(7')), 13.6 (CH$_3$(7'')), 13.5 (CH$_3$(6''')) ppm.

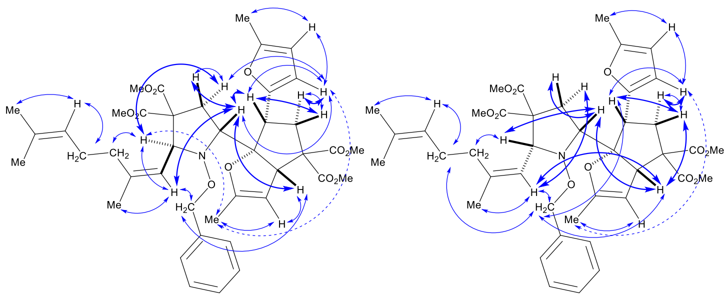
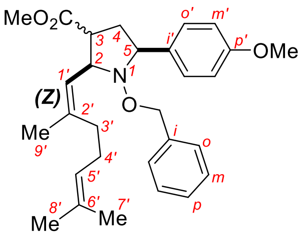


**Figure S7.** Key nOe interactions for the isomers of **11** from the NOESY data

## 8. General synthetic procedure and spectroscopic data for *N*-benzyloxypyrrolidine 12

The vial equipped with stirring bar was charged with solution of *Z*-**10a** (100 mg, 0.192 mmol), dry LiCl (20 mg, 0.48 mmol, 2.5 equiv.), $H_2O$ (8.7 µL, 0.48 mmol, 2.5 equiv.) in DMSO (4 mL). The reaction mixture was then heated at 130 °C for 20 min under microwave irradiation (150 W). This reaction was carried out 6 times on the same scale and the individual reaction mixtures were combined and were poured into 30 mL of $H_2O$ followed by the extraction with EtOAc (3×20 mL). The combined extracts were then washed with $H_2O$ (5×20 mL) and brine, dried over anhydrous $Na_2SO_4$ and evaporated. The residue was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate 10:1) to afford title compounds **12**.

**Methyl (2*RS*,5*RS*)-1-(benzyloxy)-2-((*Z*)-2,6-dimethylhepta-1,5-dien-1-yl)-5-(4-methoxyphenyl)pyrrolidine-3-carboxylate (12)**




The title compound was prepared as a mixture of diastereomers, *trans,trans*/*cis,cis* 5.4:1, in 275 mg yield (52%; dr of analytical sample: 4.3:1). Eluent: petroleum ether/EtOAc 10:1. Brownish thick oil, $R_f$ = 0.65 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{29}H_{38}NO_4^+$ $[M+H]^+$ 464.2795, found: 464.2787. *Trans,trans*-**12**, major: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.7 Hz, 2H, 2×H(*o'*)), 7.20–7.12 (m, 3H, 2×H(*m*), H(*p*)), 7.00–6.92 (m, 2H, 2×H(*o*)), 6.87 (d, *J* = 8.7 Hz, 2H, 2×H(*m'*)), 5.27 (dq, $^3J_{2,1'}$ = 9.8 Hz, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 5.17–5.05 (m, 1H, H(5')), 4.44 and 4.20 (two doublets, $^2J_{HH}$ = 10.2 Hz, 2H, $CH_2$, Bn), 4.03 (dd, $^3J_{2,1'}$ = 9.8, $^3J_{2,3}$ = 9.2 Hz, 1H, H(2)), 4.02 (dd, $^3J_{4b,5}$ = 10.4, $^3J_{4a,5}$ = 8.4 Hz, 1H, H(5)), 3.80 (s, 3H, OMe), 3.66 (s, 3H, $CO_2Me$), 2.77 (ddd, $^3J_{3,4b}$ = 11.0, $^3J_{2,3}$ = 9.2, $^3J_{3,4a}$ = 5.0 Hz, 1H, H(3)), 2.35 (ddd, $^2J_{4a,4b}$ = 13.3, $^3J_{4a,5}$ = 8.4, $^3J_{3,4a}$ = 5.0 Hz, 1H, $H_{anti}$(4a)), 2.28–2.14 (m, 1H, H(3'a)), 2.14–1.90 (m, 3H, H(3'b), $CH_2$(4')), 2.03 (ddd, $^2J_{4a,4b}$ = 13.3, $^3J_{3,4b}$ = 11.0, $^3J_{4b,5}$ = 10.4 Hz, 1H, $H_{syn}$(4b)), 1.77 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.65 (br.s, 3H, $CH_3$(8')), 1.56 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 174.5 (COO), 159.0 (C(*p'*)), 140.7 (C(2')), 137.2 (C(*i*)), 133.2 (C(*i'*)), 131.4 (C(6')), 129.1 (2×CH(*o'*)), 128.8 (2×CH(*o*)), 127.9 (2×CH(*m*)), 127.5 (CH(*p*)), 125.0 (CH(1')), 124.2 (CH(5')), 113.6 (2×CH(*m'*)), 76.9 ($CH_2$, Bn), 69.7 (CH(5)), 67.7 (CH(2)), 55.1 (OMe), 51.8 ($CO_2Me$), 44.9 (CH(3)), 33.1 ($CH_2$(4)), 32.4 ($CH_2$(3')), 27.1 ($CH_2$(4')), 25.5 ($CH_3$(8')), 23.7 ($CH_3$(9')), 17.6 ($CH_3$(7')) ppm. *Cis,cis*-**12**, minor: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.7 Hz, 2H, 2×H(*o'*)), 7.20–7.12 (m, 3H, 2×H(*m*), H(*p*)), 7.00–6.92 (m, 2H, 2×H(*o*)), 6.89 (d, *J* = 8.7 Hz, 2H, 2×H(*m'*)), 5.23 (dq, $^3J_{2,1'}$ = 9.8 Hz, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 5.17–5.05 (m, 1H, H(5')), 4.46 and 4.20 (two doublets, $^2J_{HH}$ = 10.2 Hz, 2H, $CH_2$, Bn), 4.08–3.97 (m, 1H, H(2)), 3.84 (dd, $^3J_{4a,5}$ = 10.3, $^3J_{4b,5}$ = 7.7 Hz, 1H, H(5)), 3.80 (s, 3H, OMe), 3.66 (s, 3H, $CO_2Me$), 3.11 (ddd, $^3J$ = 9.9, $^3J$ = 9.3, $^3J$ = 7.3 Hz, 1H, H(3)), 2.28–2.14 (m, 3H, $CH_2$(4), H(3'a)), 2.14–1.90 (m, 3H, H(3'b), $CH_2$(4')), 1.74 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(9')), 1.67 (br.s, 3H, $CH_3$(8')), 1.59 (br.s, 3H, $CH_3$(7')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 174.3 (COO), 159.7 (C(*p'*)), 140.1 (C(2')), 137.2 (C(*i*)), 133.4 (C(*i'*)), 131.6 (C(6')), 129.3 (2×CH(*o'*)), 128.8 (2×CH(*o*)), 127.9 (2×CH(*m*)), 127.5 (CH(*p*)), 124.0 (CH(5')), 123.1 (CH(1')), 113.5 (2×CH(*m'*)), 77.2 ($CH_2$, Bn), 69.9 (CH(5)), 66.1 (CH(2)), 55.1 (OMe), 51.3 ($CO_2Me$), 43.6 (CH(3)), 32.9 ($CH_2$(4)), 32.5 ($CH_2$(3')), 26.6 ($CH_2$(4')), 25.5 ($CH_3$(8')), 23.6 ($CH_3$(9')), 17.6 ($CH_3$(7')) ppm.

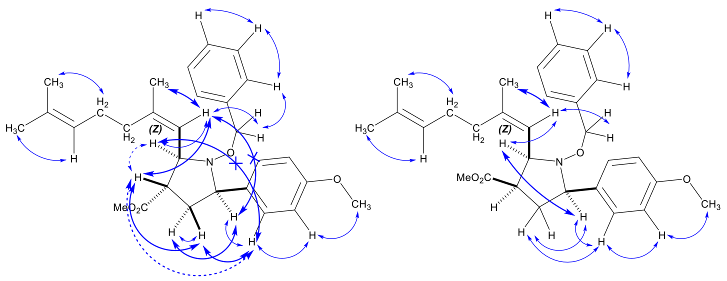
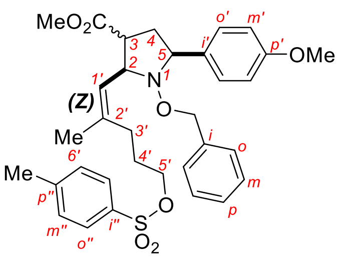


**Figure S8.** Key nOe interactions for the isomers of **12** from the NOESY data

## 9. General synthetic procedure and spectroscopic data for tosylate 13

A solution of **12** (180 mg, 0.388 mmol) in $CH_2Cl_2$/MeOH 1:1 mixture (150 mL) was cooled to -78 °C, and a stream of ozone gas (38–40 mg $O_3$/L, 18 L/h) was passed through the stirred solution for 2 min until full consumption of starting material (TLC control). Then, the ozone flow was discontinued, and argon was bubbled through the solution for 2 min. $NaBH_4$ (150 mg, 3.88 mmol, 10 equiv.) was added in one portion, and the mixture was allowed to warm to room temperature. After stirring at room temperature for an additional 1 h, the solvent was removed under reduced pressure, EtOAc (30 mL) and brine (40 mL) were added, and the aqueous phase was extracted with EtOAc (3×30 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The residue was purified by flash chromatography ($SiO_2$, petroleum ether/ethyl acetate 1:1) to obtain 68 mg of an alcohol, which was then dissolved in $CH_2Cl_2$ (8 ml) with TsCl (88 mg, 0.462 mmol, 1.5 equiv.), $Et_3N$ (90 µL, 0.62 mmol, 2 equiv.). DMAP (4 mg, 0.03 mmol, 10 mol. %) and left overnight under stirring at room temperature. After that, the reaction mixture was evaporated, the residue was purified by flash chromatography ($SiO_2$, petroleum ether/ethyl acetate 2:1) to obtain title compound **13**.

**Methyl (2*RS*,5*RS*)-1-(benzyloxy)-5-(4-methoxyphenyl)-2-((*Z*)-2-methyl-5-(tosyloxy)pent-1-en-1-yl)pyrrolidine-3-carboxylate (13)**

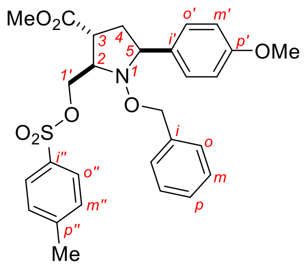



The title compound was prepared as a mixture of diastereomers, *trans,trans*/*cis,cis* 2.6:1, in 73 mg yield (36%). Colorless thick oil, $R_f$ = 0.33 (petroleum ether–EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{33}H_{40}NO_7S^+$ $[M+H]^+$ 594.2520, found: 594.2519. *Trans,trans*-**13**, major: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.77 (d, $J$ = 8.3 Hz, 2H, 2×H(*o"*)), 7.36 (d, $J$ = 8.7 Hz, 2H, 2×H(*o'*)), 7.32 (d, $J$ = 8.2 Hz, 2H, 2×H(*m"*)), 7.20–7.12 (m, 3H, 2×H(*m*), H(*p*)), 6.92–6.85 (m, 2H, 2×H(*o*)), 6.88 (d, $J$ = 8.7 Hz, 2H, 2×H(*m'*)), 5.25 (dq, $^3J_{2,1'}$ = 9.7 Hz, $^4J_{1',9'}$ = 1.4 Hz, 1H, H(1')), 4.34 and 4.15 (two doublets, $^2J_{HH}$ = 10.2 Hz, 2H, $CH_2$, Bn), 4.05–3.86 (m, 2H, $CH_2$(5')), 3.96 (dd, $^3J_{4b,5}$ = 11.3, $^3J_{4a,5}$ = 9.4 Hz, 1H, H(5)), 3.90 (dd, $^3J_{2,1'}$ = 9.7, $^3J_{2,3}$ = 9.1 Hz, 1H, H(2)), 3.83 (s, 3H, OMe), 3.65 (s, 3H, $CO_2Me$), 2.74 (ddd, $^3J_{3,4b}$ = 11.1, $^3J_{2,3}$ = 9.3, $^3J_{3,4a}$ = 5.0 Hz, 1H, H(3)), 2.43 (s, 3H, C(*p*)–Me), 2.37–1.90 (m, 3H, $H_{syn}$(4b), $CH_2$(3')), 2.32 (ddd, $^2J_{4a,4b}$ = 13.3, $^3J_{4a,5}$ = 8.3, $^3J_{3,4a}$ = 5.0 Hz, 1H, $H_{anti}$(4a)), 1.78–1.63 (m, 2H, $CH_2$(4')), 1.70 (d, $^4J_{1',9'}$ = 1.4 Hz, 3H, $CH_3$(6')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 174.4 (COO), 159.1 (C(*p'*)), 144.6 (C(*p"*)), 139.1 (C(2')), 137.0 (C(*i*)), 133.2 and 133.0 (C(*i'*) and C(*i"*)), 129.8 (2×CH(*m"*)), 129.1 (2×CH(*o'*)), 128.9 (2×CH(*o*)), 128.0 and 127.8 (2×CH(*m*) and 2×CH(*o"*)), 127.6 (CH(*p*)), 126.0 (CH(1')), 113.6 (2×CH(*m'*)), 76.9 ($CH_2$, Bn), 70.4 ($CH_2$(5')), 69.7 (CH(5)), 67.4 (CH(2)), 55.2 (OMe), 52.0 ($CO_2Me$), 44.7 (CH(3)), 33.1 ($CH_2$(4)), 28.0 ($CH_2$(3')), 27.7 ($CH_2$(4')), 23.6 ($CH_3$(6')), 21.6 (C(*p*)–<u>Me</u>) ppm. *Cis,cis*-**13**, minor: $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.78 (d, $J$ = 8.2 Hz, 2H, 2×H(*o"*)), 7.48 (d, $J$ = 8.7 Hz, 2H, 2×H(*o'*)), 7.32 (d, $J$ = 8.2 Hz, 2H, 2×H(*m"*)), 7.20–7.12 (m, 3H, 2×H(*m*), H(*p*)), 6.92–6.85 (m, 2H, 2×H(*o*)), 6.90 (d, $J$ = 8.7 Hz, 2H, 2×H(*m'*)), 5.21 (dq, $^3J_{2,1'}$ = 9.7 Hz, $^4J_{1',9'}$ = 1.4 Hz, 1H, H(1')), 4.37 and 4.16 (two doublets, $^2J_{HH}$ = 10.2 Hz, 2H, $CH_2$, Bn), 4.05–3.86 (m, 2H, $CH_2$(5')), 3.91 (t, $^3J_{2,1'}$ = $^3J_{2,3}$ = 9.7 Hz, 1H, H(2)), 3.86–3.78 (m, 1H, H(5)), 3.82 (s, 3H, OMe), 3.65 (s, 3H, $CO_2Me$), 3.07 (td, $^3J$ = 9.7, $^3J$ = 7.3 Hz, 1H, H(3)), 2.43 (s, 3H, C(*p*)–Me), 2.37–1.90 (m, 4H, $CH_2$(4), $CH_2$(3')), 1.78–1.63 (m, 2H, $CH_2$(4')), 1.67 (d, $^4J_{1',9'}$ = 1.4 Hz, 3H, $CH_3$(6')) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 173.7 (COO), 159.1 (C(*p'*)), 144.6 (C(*p"*)), 138.4 (C(2')), 137.2 (C(*i*)), 133.2 and 133.0 (C(*i'*) and C(*i"*)), 129.8 (2×CH(*m"*)), 129.4 (2×CH(*o'*)), 128.9 (2×CH(*o*)), 128.0 and 127.8 (2×CH(*m*) and 2×CH(*o"*)), 127.6 (CH(*p*)), 124.3 (CH(1')), 113.6 (2×CH(*m'*)), 77.1 ($CH_2$, Bn), 70.2 ($CH_2$(5')), 69.9 (CH(5)), 65.9 (CH(2)), 55.2 (OMe), 51.5 ($CO_2Me$), 43.4 (CH(3)), 32.8 ($CH_2$(4)), 28.1 ($CH_2$(3')), 27.4 ($CH_2$(4')), 23.5 ($CH_3$(6')), 21.6 (C(*p*)–<u>Me</u>) ppm.

## 10. General synthetic procedure and spectroscopic data for tosylate 14

A solution of **12** (90 mg, 0.194 mmol) and pyridine (50 µL, 0.582 mmol, 3 equiv.) in $CH_2Cl_2$/MeOH 1:1 mixture (100 mL) was cooled to -78 °C, and a stream of ozone gas (40–50 mg $O_3$/L, 18 L/h) was passed through the stirred solution for 4 min until full consumption of starting material (TLC control). Then, the ozone flow was discontinued, and argon was bubbled through the solution for 2 min. $NaBH_4$ (75 mg, 1.94 mmol, 10 equiv.) was added in one portion, and the mixture was allowed to warm to room temperature. After stirring at room temperature for an additional 1 h, the solvent was removed under reduced pressure, EtOAc (20 mL) and brine (20 mL) were added, and the aqueous phase was extracted with EtOAc (3×20 mL). The combined organic extracts were dried over anhydrous $Na_2SO_4$ and evaporated under reduced pressure. The residue was purified by flash chromatography ($SiO_2$, petroleum ether/ethyl acetate 1:1) to obtain 46 mg of a mixture, which was then dissolved in $CH_2Cl_2$ (4 ml) with TsCl (30 mg, 0.157 mmol, 1.3 equiv.), $Et_3N$ (30 µL, 0.21 mmol, 1.7 equiv.). DMAP (1.5 mg, 0.01 mmol, 10 mol. %) and left overnight under stirring at room temperature. After that, the reaction mixture was evaporated, the residue was purified by flash chromatography ($SiO_2$, petroleum ether/ethyl acetate 2:1) to obtain a mixture of **14** and **13**.

**Methyl (2*RS*,3*RS*,5*SR*)-1-(benzyloxy)-5-(4-methoxyphenyl)-2-((tosyloxy)methyl)pyrrolidine-3-carboxylate (14)**



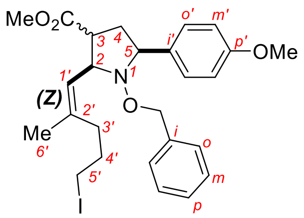

Obtained as a mixture of **14** and **13** (dr 1.1:1), 38 mg (3:1 mol., 27% and 9% , $^1$H NMR), colorless thick oil. **14**: $R_f$ = 0.33 (petroleum ether–EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{28}H_{32}NO_7S^+$ $[M+H]^+$ 526.1894, found: 526.1892. $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.3 Hz, 2H, 2×H(*o''*)), 7.36 (d, *J* = 8.7 Hz, 2H, 2×H(*o'*)), 7.33 (d, *J* = 8.2 Hz, 2H, 2×H(*m''*)), 7.22–7.14 (m, 3H, 2×H(*m*), H(*p*)), 6.95–6.85 (m, 4H, 2×H(*o*), 2×H(*m'*)), 4.21 (dd, $^2J_{1'a,1'b}$ = 10.3, $^3J_{2,1'a}$ = 4.2 Hz, 1H, H(1'a)), 4.17 (dd, $^2J_{1'a,1'b}$ = 10.3, $^3J_{2,1'b}$ = 3.7 Hz, 1H, H(1'b)), 4.19 and 4.05 (two doublets, $^2J_{HH}$ = 10.2 Hz, 2H, $CH_2$, Bn), 3.98 (dd, $^3J_{4b,5}$ = 11.1, $^3J_{4a,5}$ = 7.7 Hz, 1H, H(5)), 3.82 (s, 3H, OMe), 3.67 (s, 3H, $CO_2Me$), 3.42 (ddd, $^3J_{2,3}$ = 8.4, $^3J_{2,1'a}$ = 4.2, $^3J_{2,1'b}$ = 3.7 Hz, 1H, H(2)), 2.97 (ddd, $^3J_{3,4b}$ = 10.9, $^3J_{2,3}$ = 8.4, $^3J_{3,4a}$ = 3.9 Hz, 1H, H(3)), 2.42 (s, 3H, C(*p*)–Me), 2.35 (ddd, $^2J_{4a,4b}$ = 13.3, $^3J_{4a,5}$ = 7.7, $^3J_{3,4a}$ = 3.9 Hz, 1H, $H_{anti}$(4a)), 2.02 (ddd, $^2J_{4a,4b}$ = 13.3, $^3J_{4b,5}$ = 11.1, $^3J_{3,4b}$ = 10.9 Hz, 1H, $H_{syn}$(4b)) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 173.8 (COO), 159.3 (C(*p'*)), 144.8 (C(*p''*)), 136.5 (C(*i*)), 132.9 (C(*i''*)), 132.3 (C(*i'*), 129.8 (2×CH(*m''*)), 129.2 (2×CH(*o'*)), 128.7 (2×CH(*o*)), 128.1 and 128.1 (2×CH(*m*) and 2×CH(*o''*)), 127.9 (CH(*p*)), 113.7 (2×CH(*m'*)), 76.9 ($CH_2$, Bn), 70.2 (CH(5)), 68.7 ($CH_2$(1')), 67.7 (CH(2)), 55.2 (OMe), 52.2 ($CO_2Me$), 39.9 (CH(3)), 32.8 ($CH_2$(4)), 21.6 (C(*p*)–Me) ppm.

## 11. General synthetic procedure and spectroscopic data for iodide 15

Preparation of $SmI_2$ (0.1 M in THF): 1,2-Diiodoethane (268 mg, 1 mmol) was dissolved in THF (10 mL), which was freshly distilled from sodium/benzophenone, and was degassed using freeze-pump-thaw technique. This solution was added to Sm powder (300 mg, 2.0 mmol), which was heated with a heat gun under reduced pressure for 10 min. The blue suspension was sonicated for 1 h at room temperature. The $SmI_2$ solution in THF was used as is (0.1 M) without titrametric determination of concentration.

A solution of $SmI_2$ in THF (0.1 M, 1.7 mL, 0.17 mmol, 10 equiv.) was added to degassed by freeze-pump-thaw technique solution of **13** (10 mg, 16.8 μmol) in THF (2 mL) at room temperature, and maintained for 12 h. This mixture was quenched with saturated aqueous $Na_2S_2O_3$ (5 mL), and extracted with EtOAc (2x 10 mL). The combined organic extracts were washed with brine (10 mL), dried over $Na_2SO_4$, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc 10:1) to obtain title compound **15**.

**Methyl (2*RS*,5*RS*)-1-(benzyloxy)-2-((*Z*)-5-iodo-2-methylpent-1-en-1-yl)-5-(4-methoxyphenyl)pyrrolidine-3-carboxylate (15)**

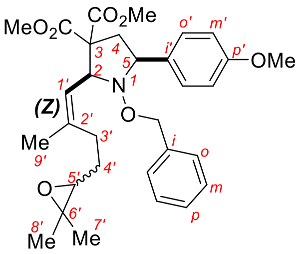



The title compound was prepared as a mixture of diastereomers, *trans,trans*/*cis,cis* 1.6:1, in 5 mg yield (54%). Yellowish thick oil, $R_f$ = 0.58 (petroleum ether–EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{26}H_{33}INO_4^+$ $[M+H]^+$ 550.1449, found: 550.1438. *Trans,trans*-**15**, major: $^1$H NMR (400.2 MHz, $CDCl_3$): δ 7.39 (d, $J$ = 8.7 Hz, 2H, 2×H(*o'*)), 7.24–7.14 (m, 3H, 2×H(*m*), H(*p*)), 6.99–6.92 (m, 2H, 2×H(*o*)), 6.89 (d, $J$ = 8.7 Hz, 2H, 2×H(*m'*)), 5.31 (dq, $^3J_{2,1'}$ = 9.4 Hz, $^4J_{1',9'}$ = 1.3 Hz, 1H, H(1')), 4.39 and 4.18 (two doublets, $^2J_{HH}$ = 10.2 Hz, 2H, $CH_2$, Bn), 4.02 (dd, $^3J_{4b,5}$ = 10.3, $^3J_{4a,5}$ = 8.4 Hz, 1H, H(5)), 4.00 (t, $^3J_{2,1'}$ = $^3J_{2,3}$ = 9.4 Hz, 1H, H(2)), 3.83 (s, 3H, OMe), 3.70 (s, 3H, $CO_2Me$), 3.21–3.04 (m, 2H, $CH_2$(5')), 2.77 (ddd, $^3J_{3,4b}$ = 10.9, $^3J_{2,3}$ = 9.4, $^3J_{3,4a}$ = 5.0 Hz, 1H, H(3)), 2.40–2.00 (m, 2H, $CH_2$(3')), 2.35 (ddd, $^2J_{4a,4b}$ = 13.3, $^3J_{4a,5}$ = 8.4, $^3J_{3,4a}$ = 5.0 Hz, 1H, $H_{anti}$(4a)), 2.05 (ddd, $^2J_{4a,4b}$ = 13.3, $^3J_{3,4b}$ = 10.9, $^3J_{4b,5}$ = 10.3 Hz, 1H, $H_{syn}$(4b)), 2.00–1.79 (m, 2H, $CH_2$(4')), 1.76 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(6')) ppm. $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ 174.5 (COO), 159.1 (C(*p'*)), 138.9 (C(2')), 137.0 (C(*i*)), 133.2 (C(*i'*)), 129.2 (2×CH(*o'*)), 128.9 (2×CH(*o*)), 128.1 (2×CH(*m*)), 127.7 (CH(*p*)), 126.2 (CH(1')), 113.7 (2×CH(*m'*)), 77.2 ($CH_2$, Bn), 69.8 (CH(5)), 67.5 (CH(2)), 55.3 (OMe), 52.2 ($CO_2Me$), 44.8 (CH(3)), 33.2 ($CH_2$(3')), 33.1 ($CH_2$(4)), 32.5 ($CH_2$(4')), 23.7 ($CH_3$(6')), 6.3 ($CH_2$(5')) ppm. *Cis,cis*-**15**, minor: $^1$H NMR (400.2 MHz, $CDCl_3$): δ 7.50 (d, $J$ = 8.7 Hz, 2H, 2×H(*o'*)), 7.24–7.14 (m, 3H, 2×H(*m*), H(*p*)), 6.99–6.92 (m, 2H, 2×H(*o*)), 6.91 (d, $J$ = 8.7 Hz, 2H, 2×H(*m'*)), 5.27 (dq, $^3J_{2,1'}$ = 9.5 Hz, $^4J_{1',9'}$ = 1.4 Hz, 1H, H(1')), 4.42 and 4.18 (two doublets, $^2J_{HH}$ = 10.2 Hz, 2H, $CH_2$, Bn), 4.04 (t, $^3J_{2,1'}$ = $^3J_{2,3}$ = 9.5 Hz, 1H, H(2)), 3.87 (dd, $^3J_{4b,5}$ = 10.8, $^3J_{4a,5}$ = 7.8 Hz, 1H, H(5)), 3.83 (s, 3H, OMe), 3.68 (s, 3H, $CO_2Me$), 3.21–3.04 (m, 3H, H(3), $CH_2$(5')), 2.40–2.00 (m, 4H, $CH_2$(4), $CH_2$(3')), 2.00–1.79 (m, 2H, $CH_2$(4')), 1.72 (d, $^4J_{1',9'}$ = 1.3 Hz, 3H, $CH_3$(6')) ppm. $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ 173.8 (COO), 159.1 (C(*p'*)), 138.4 (C(2')), 137.1 (C(*i*)), 133.1 (C(*i'*)), 129.4 (2×CH(*o'*)), 128.9 (2×CH(*o*)), 128.1 (2×CH(*m*)), 127.7 (CH(*p*)), 124.5 (CH(1')), 113.6 (2×CH(*m'*)), 77.1 ($CH_2$, Bn), 70.0 (CH(5)), 66.0 (CH(2)), 55.3 (OMe), 51.5 ($CO_2Me$), 43.6 (CH(3)), 32.9 ($CH_2$(3')), 32.8 ($CH_2$(4)), 31.9 ($CH_2$(4')), 23.6 ($CH_3$(6')), 6.6 ($CH_2$(5')) ppm.

## 12. General synthetic procedure and spectroscopic data for epoxide 16

A solution of *Z*-**10a** (20 mg, 0.038 mmol) in $CH_2Cl_2$ (1 mL) was cooled to 0 °C, then mCPBA (85%, 9.5 mg, 0.046 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at room temperature for 12 h, then washed with saturated $NaHCO_3$ solution, the organic extract was dried over anhydrous $Na_2SO_4$ and evaporated. The residue was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate/$Et_3N$ 100:3:1→100:20:1) to afford title compound **16**.

**Dimethyl (2*RS*,5*RS*)-1-(benzyloxy)-2-((*Z*)-4-(3,3-dimethyloxiran-2-yl)-2-methylbut-1-en-1-yl)-5-(4-methoxyphenyl)pyrrolidine-3,3-dicarboxylate (16)**

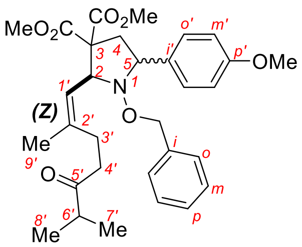



The title compound was prepared as a mixture of diastereomers, dr **A**/**B** 1:1, in 18 mg yield (88%). Colorless thick oil, $R_f$ = 0.32 (petroleum ether/EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{31}H_{40}NO_7^+$ $[M+H]^+$ 538.2800, found: 538.2796. $^1$H NMR (300.1 MHz, $CDCl_3$): δ 7.47 and 7.46 (two d, *J* = 8.7 Hz, 4H, 2×H(*o'*)$_\mathbf{A}$, 2×H(*o'*)$_\mathbf{B}$), 7.20–7.14 (m, 6H, 2×H(*m*)$_\mathbf{A}$, 2×H(*m*)$_\mathbf{B}$, H(*p*)$_\mathbf{A}$, H(*p*)$_\mathbf{B}$), 6.96–6.86 (m, 4H, 2×H(*o*)$_\mathbf{A}$, 2×H(*o*)$_\mathbf{B}$), 6.89 (two d, *J* = 8.7 Hz, 4H, 2×H(*m'*)$_\mathbf{A}$, 2×H(*m'*)$_\mathbf{B}$), 5.13 and 5.13 (two br.d, $^3J_{2,1'}$ = 10.0 Hz, 2H, H(1')$_\mathbf{A}$, H(1')$_\mathbf{B}$), 4.58 and 4.58 (two d, $^3J_{2,1'}$ = 9.9 Hz, 2H, H(2)$_\mathbf{A}$, H(2)$_\mathbf{B}$), 4.38, 4.38, 4.16, 4.15 (four d, $^2J_{HH}$ = 10.2 Hz, 4H, 2×$CH_2$, Bn$_\mathbf{A}$, Bn$_\mathbf{B}$),3.86 and 3.85 (two dd, $^3J_{4a,5}$ = 11.5, $^3J_{4b,5}$ = 7.4 Hz, 2H, H(5)$_\mathbf{A}$, H(5)$_\mathbf{B}$), 3.83 and 3.83 (two s, 6H, OMe$_\mathbf{A}$, OMe$_\mathbf{B}$), 3.75, 3.74, 3.73 and 3.73 (four s, 12H, 2 $CO_2Me_\mathbf{A}$, 2 $CO_2Me_\mathbf{B}$), 2.81 and 2.81 (two dd, $^2J_{4a,4b}$ = 13.7, $^3J_{4a,5}$ = 11.5 Hz, 2H, $H_{syn}$(4a)$_\mathbf{A}$, $H_{syn}$(4a)$_\mathbf{B}$), 2.75 and 2.73 (two t, $^3J_{4',5'}$ = 6.0 Hz, 2H, H(5')$_\mathbf{A}$, H(5')$_\mathbf{B}$), 2.43 and 2.42 (two dd, $^2J_{4a,4b}$ = 13.7, $^3J_{4b,5}$ = 7.4 Hz, 2H, $H_{anti}$(4b)$_\mathbf{A}$, $H_{anti}$(4b)$_\mathbf{B}$), 2.48–2.21 (m, 4H, $CH_2$(3')$_\mathbf{A}$, $CH_2$(3')$_\mathbf{B}$), 1.77 and 1.76 (two d, $^4J_{1',9'}$ = 1.1 Hz, 6H, $CH_3$(9')$_\mathbf{A}$, $CH_3$(9')$_\mathbf{B}$), 1.72–1.52 (m, 4H, $CH_2$(4')$_\mathbf{A}$, $CH_2$(4')$_\mathbf{B}$), 1.27 and 1.26 (two s, 6H, $CH_3$(8')$_\mathbf{A}$, $CH_3$(8')$_\mathbf{B}$), 1.23 and 1.22 (two s, 6H, $CH_3$(7')$_\mathbf{A}$, $CH_3$(7')$_\mathbf{B}$) ppm. $^{13}$C NMR (75.5 MHz, $CDCl_3$): δ 171.5, 171.5, 170.2 and 170.2 (2 COO$_\mathbf{A}$, 2 COO$_\mathbf{B}$), 159.3 (C(*p'*)$_\mathbf{A}$, C(*p'*)$_\mathbf{B}$), 141.1 and 141.0 (C(2')$_\mathbf{A}$, C(2')$_\mathbf{B}$), 137.0 and 137.0 (C(*i*)$_\mathbf{A}$, C(*i*)$_\mathbf{B}$), 132.3 and 132.3 (C(*i'*)$_\mathbf{A}$, C(*i'*)$_\mathbf{B}$), 129.4 (2×CH(*o'*)$_\mathbf{A}$, 2×CH(*o'*)$_\mathbf{B}$), 129.0 and 129.0 (2×CH(*o*)$_\mathbf{A}$, 2×CH(*o*)$_\mathbf{B}$), 127.9 (2×CH(*m*)$_\mathbf{A}$, 2×CH(*m*)$_\mathbf{B}$), 127.6 and 127.6 (CH(*p*)$_\mathbf{A}$, CH(*p*)$_\mathbf{B}$), 122.6 and 122.6 (CH(1')$_\mathbf{A}$, CH(1')$_\mathbf{B}$), 113.6 (2×CH(*m'*)$_\mathbf{A}$, 2×CH(*m'*)$_\mathbf{B}$), 77.2 ($CH_2$, Bn$_\mathbf{A}$, Bn$_\mathbf{B}$), 68.6 and 68.5 (CH(5)$_\mathbf{A}$, CH(5)$_\mathbf{B}$), 68.3 and 68.2 (CH(2)$_\mathbf{A}$, CH(2)$_\mathbf{B}$), 64.2 and 64.2 (CH(5')$_\mathbf{A}$, CH(5')$_\mathbf{B}$), 59.5 and 59.4 (C(3)$_\mathbf{A}$, C(3)$_\mathbf{B}$), 58.3 and 58.3 (C(6')$_\mathbf{A}$, C(6')$_\mathbf{B}$), 55.3 (OMe$_\mathbf{A}$, OMe$_\mathbf{B}$), 52.9, 52.8, 52.4 and 52.4 (2 $CO_2Me_\mathbf{A}$, 2 $CO_2Me_\mathbf{B}$), 37.9 and 37.9 ($CH_2$(4)$_\mathbf{A}$, $CH_2$(4)$_\mathbf{B}$), 29.1 and 29.0 ($CH_2$(3')$_\mathbf{A}$, $CH_2$(3')$_\mathbf{B}$), 27.9 and 27.6 ($CH_2$(4')$_\mathbf{A}$, $CH_2$(4')$_\mathbf{B}$), 24.8 and 24.9 ($CH_3$(8')$_\mathbf{A}$, $CH_3$(8')$_\mathbf{B}$), 23.9 and 23.9 ($CH_3$(9')$_\mathbf{A}$, $CH_3$(9')$_\mathbf{B}$), 18.6 and 18.6 ($CH_3$(7')$_\mathbf{A}$, $CH_3$(7')$_\mathbf{B}$) ppm.

## 13. General synthetic procedure and spectroscopic data for ketone 17 and aldehyde 18

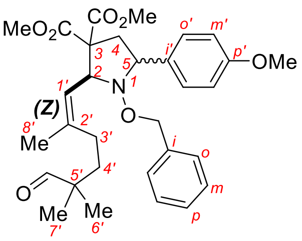
A solution of **16** (10 mg, 0.019 mmol) and $BF_3{\cdot}Et_2O$ (4.7 µL, 0.038 mmol, 2 equiv.) in 1,2-dichloroethane (1 mL) was heated at 60 °C and stirred for 5 h. After that, the reaction mixture was passed through a short pad of silica gel, the solvent was removed under reduced pressure. The residue was purified by column chromatography ($SiO_2$, petroleum ether/ethyl acetate 5:1→3:1) to obtain 8 mg (total yield 80%) of a mixture of **17** (68%, $^{1}$H NMR) and **18** (12%, $^{1}$H NMR). Colorless thick oil, $R_f$ = 0.35 (petroleum ether–EtOAc 3:1). HRMS (ESI) *m/z*: calcd for $C_{31}H_{40}NO_7^+$ $[M+H]^+$ 538.2800, found: 538.2802.

### Dimethyl (*Z*)-1-(benzyloxy)-2-(2,6-dimethyl-5-oxohept-1-en-1-yl)-5-(4-methoxyphenyl)pyrrolidine-3,3-dicarboxylate (17)




Mixture of diastereomers, *cis*/*trans* 1.2:1. *Cis*-**17**: $^{1}$H NMR (600.1 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.7 Hz, 2H, 2×H(*o'*)), 7.25–7.15 (m, 3H, 2×H(*m*), H(*p*)), 6.98–6.92 (m, 2H, 2×H(*o*)), 6.89 (d, *J* = 8.7 Hz, 2H, 2×H(*m'*)), 5.14 (dq, $^{3}J_{2,1'}$ = 10.0, $^{4}J_{1',9'}$ = 1.4 Hz, 1H, H(1')), 4.48 (d, $^{3}J_{2,1'}$ = 10.0 Hz, 1H, H(2)), 4.37 and 4.16 (two doublets, $^{2}J_{HH}$ = 10.3 Hz, 2H, $CH_2$, Bn), 3.85 (dd, $^{3}J_{4a,5}$ = 11.5, $^{3}J_{4b,5}$ = 7.5 Hz, 1H, H(5)), 3.82 (s, 3H, OMe), 3.75 and 3.74 (both s, 2×3H, 2 $CO_2Me$), 2.78 (dd, $^{2}J_{4a,4b}$ = 13.8, $^{3}J_{4a,5}$ = 11.5 Hz, 1H, $H_{syn}$(4a)), 2.60–2.30 (m, 4H, $CH_2$(3'), $CH_2$(4')), 2.56 (sept, $^{3}J_{6',7'}$ = $^{3}J_{6',8'}$ = 7.0 Hz, 1H, H(6')), 2.46 (dd, $^{2}J_{4a,4b}$ = 13.8, $^{3}J_{4b,5}$ = 7.5 Hz, 1H, $H_{anti}$(4b)), 1.73 (d, $^{4}J_{1',9'}$ = 1.4 Hz, 3H, $CH_3$(9')), 1.10 and 1.09 (two d, $^{3}J_{6',7'}$ = $^{3}J_{6',8'}$ = 7.0 Hz, 6H, $CH_3$(7'), $CH_3$(8')) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): δ 213.8 (C(5')), 171.4 and 170.3 (2 COO), 159.3 (C(*p'*)), 141.2 (C(2')), 137.1 (C(*i*)), 132.4 (C(*i'*)), 129.4 (2×CH(*o'*)), 128.9 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.7 (CH(*p*)), 122.6 (CH(1')), 113.7 (2×CH(*m'*)), 77.2 ($CH_2$, Bn), 68.6 (CH(5)), 68.5 (CH(2)), 59.3 (C(3)), 55.3 (OMe), 52.9 and 52.5 (2 $CO_2Me$), 40.8 (CH(6')), 37.9 ($CH_2$(4)), 39.1 ($CH_2$(4')), 26.3 ($CH_2$(3')), 23.9 ($CH_3$(9')), 18.3 and 18.2 ($CH_3$(7'), $CH_3$(8')) ppm. *Trans*-**17**: $^{1}$H NMR (600.1 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.7 Hz, 2H, 2×H(*o'*)), 7.25–7.15 (m, 3H, 2×H(*m*), H(*p*)), 7.11–7.05 (m, 2H, 2×H(*o*)), 6.85 (d, *J* = 8.7 Hz, 2H, 2×H(*m'*)), 5.24 (br.d, $^{3}J_{2,1'}$ = 10.5, 1H, H(1')), 5.11 (br.d, $^{3}J_{2,1'}$ = 10.5, 1H, H(2)), 4.37–4.33 (m, 1H, H(5)), 4.35 and 4.33 (two doublets, $^{2}J_{HH}$ = 11.2 Hz, 2H, $CH_2$, Bn), 3.81 (s, 3H, OMe), 3.75 and 3.63 (both s, 2×3H, 2 $CO_2Me$), 3.04 (dd, $^{2}J_{4a,4b}$ = 13.7, $^{3}J_{4a,5}$ = 8.0 Hz, 1H, $H_{syn}$(4a)), 2.60–2.30 (m, 4H, $H_{anti}$(4b), H(3'a), $CH_2$(4')), 2.44 (sept, $^{3}J_{6',7'}$ = $^{3}J_{6',8'}$ = 7.0 Hz, 1H, H(6')), 2.27–2.18 (m, 1H, H(3'b)), 1.72 (d, $^{4}J_{1',9'}$ = 1.4 Hz, 3H, $CH_3$(9')), 1.02 and 0.99 (two d, $^{3}J_{6',7'}$ = $^{3}J_{6',8'}$ = 7.0 Hz, 6H, $CH_3$(7'), $CH_3$(8')) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): δ 214.4 (C(5')), 171.3 and 169.8 (2 COO), 159.0 (C(*p'*)), 141.2 (C(2')), 137.5 (C(*i*)), 131.8 (br.s, C(*i'*)), 129.4 (2×CH(*o'*)), 128.8 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.6 (CH(*p*)), 119.4 (br.s, CH(1')), 113.5 (2×CH(*m'*)), 75.7 ($CH_2$, Bn), 68.5 (CH(2)), 67.4 (br.s, CH(5) and C(3)), 55.3 (OMe), 52.9 and 52.5 (2 $CO_2Me$), 40.7 (CH(6')), 36.7 ($CH_2$(4)), 38.6 ($CH_2$(4')), 26.1 ($CH_2$(3')), 23.8 ($CH_3$(9')), 18.2 and 18.2 ($CH_3$(7'), $CH_3$(8')) ppm.

### Dimethyl (*Z*)-1-(benzyloxy)-5-(4-methoxyphenyl)-2-(2,5,5-trimethyl-6-oxohex-1-en-1-yl)pyrrolidine-3,3-dicarboxylate (18)




Mixture of diastereomers, *cis*/*trans* 1.8:1. *Cis*-**18**: $^{1}$H NMR (600.1 MHz, $CDCl_3$): δ 9.40 (s, 1H, CHO), 7.47 (d, *J* = 8.7 Hz, 2H, 2×H(*o'*)), 7.25–7.15 (m, 3H, 2×H(*m*), H(*p*)), 6.98–6.92 (m, 2H, 2×H(*o*)), 6.89 (d, *J* = 8.7 Hz, 2H, 2×H(*m'*)), 5.13–5.08 (m, 1H, H(1')), 4.49 (d, $^{3}J_{2,1'}$ = 10.1 Hz, 1H, H(2)), 4.37 and 4.16 (two doublets, $^{2}J_{HH}$ = 10.3 Hz, 2H, $CH_2$, Bn), 3.88–3.82 (m, 1H, H(5)), 3.83 (s, 3H, OMe), 3.75 and 3.72 (both s, 2×3H, 2 $CO_2Me$), 2.79 (dd, $^{2}J_{4a,4b}$ = 13.7, $^{3}J_{4a,5}$ = 11.6 Hz, 1H, $H_{syn}$(4a)), 2.60–2.30 (m, 1H, $H_{anti}$(4b)), 2.27–2.18 (m, 1H, H(3'a)), 2.00–1.93 (m, 1H, H(3'b)), 1.74–1.71 (m, 3H, $CH_3$(8')), 1.53–1.45 (m, 2H, $CH_2$(4')), 1.01 (s, 6H, $CH_3$(6'), $CH_3$(7')) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$): δ 206.4 (CHO), 171.5 and 170.2 (2 COO), 159.3 (C(*p'*)), 141.4 (C(2')), 137.1 (C(*i*)), 132.3 (C(*i'*)), 129.4 (2×CH(*o'*)), 128.9 (2×CH(*o*)), 128.0 (2×CH(*m*)), 127.7 (CH(*p*)), 122.4 (CH(1')), 113.7 (2×CH(*m'*)), 77.2 ($CH_2$, Bn), 68.6 (CH(5)), 68.3 (CH(2)), 59.5 (C(3)), 55.3 (OMe), 52.9 and 52.4 (2 $CO_2Me$), 45.8 (C(5')), 37.9 ($CH_2$(4)), 35.4 ($CH_2$(4')), 26.9 ($CH_2$(3')), 23.8 ($CH_3$(8')), 20.9 ($CH_3$(6'), $CH_3$(7')) ppm. *Trans*-**17**: $^{1}$H NMR (600.1 MHz, $CDCl_3$): δ 9.46, 7.30 (d, *J* = 8.7 Hz, 2H, 2×H(*o'*)), 7.25–7.15 (m, 3H, 2×H(*m*), H(*p*)), 7.11–7.05 (m, 2H, 2×H(*o*)), 6.85 (d, *J* = 8.7 Hz, 2H, 2×H(*m'*)), 5.27–5.19 (m, 1H, H(1')), 5.13–5.08 (m, 1H, H(2)), 4.40–4.27 (m, 3H, H(5), $CH_2$(Bn)), 3.81 (s, 3H, OMe), 3.75 and 3.60 (both s, 2×3H, 2 $CO_2Me$), 3.07–3.00 (m, 1H, $H_{syn}$(4a)), 2.60–2.30 (m, 1H, $H_{anti}$(4b)), 2.27–2.18 (m, 1H, H(3'a)), 1.90–1.85 (m, 1H, H(3'b)), 1.74–1.71 (m, 3H, $CH_3$(8')), 1.53–1.45 (m, 2H, $CH_2$(4')), 1.07 (s, 6H, $CH_3$(6'), $CH_3$(7')) ppm. $^{13}C$ NMR (150.9 MHz, $CDCl_3$): δ 206.0 (CHO), 171.3 and 169.8 (2 COO), 159.0 (C(*p'*)), 141.4 (C(2')), 137.5 (C(*i*)), 129.4 (2×CH(*o'*)), 128.8 (2×CH(*o*)), 128.1 (2×CH(*m*)), 127.6 (CH(*p*)), 119.4 (br.s, CH(1')), 113.5 (2×CH(*m'*)), 75.8 ($CH_2$, Bn), 55.3 (OMe), 52.9 and 52.5 (2 $CO_2Me$), 45.7 (C(5')), 36.7 ($CH_2$(4)), 35.3 ($CH_2$(4')), 26.8 ($CH_2$(3')), 23.8 ($CH_3$(8')), 21.1 ($CH_3$(6'), $CH_3$(7')) ppm. Signals corresponding to CH(2), C(3), CH(5), C(*i'*) atoms in $^{13}C$ NMR were not detected either due to broadening caused by dynamic conformational effects or/and due to overlap with more intense signals of mixture components.

## 14. References


[S1] J. Wang, J. Yin, H. Imtiaz, H. Wang, Y. Li. *J. Am. Chem. Soc.* **2024**, *146*, 25078.

[S2] C. Arbonés, F.J. Sánchez, M.-P. Marco, F. Camps, A. Messeguer. *Heterocycles*, **1990**, *31*, 67.

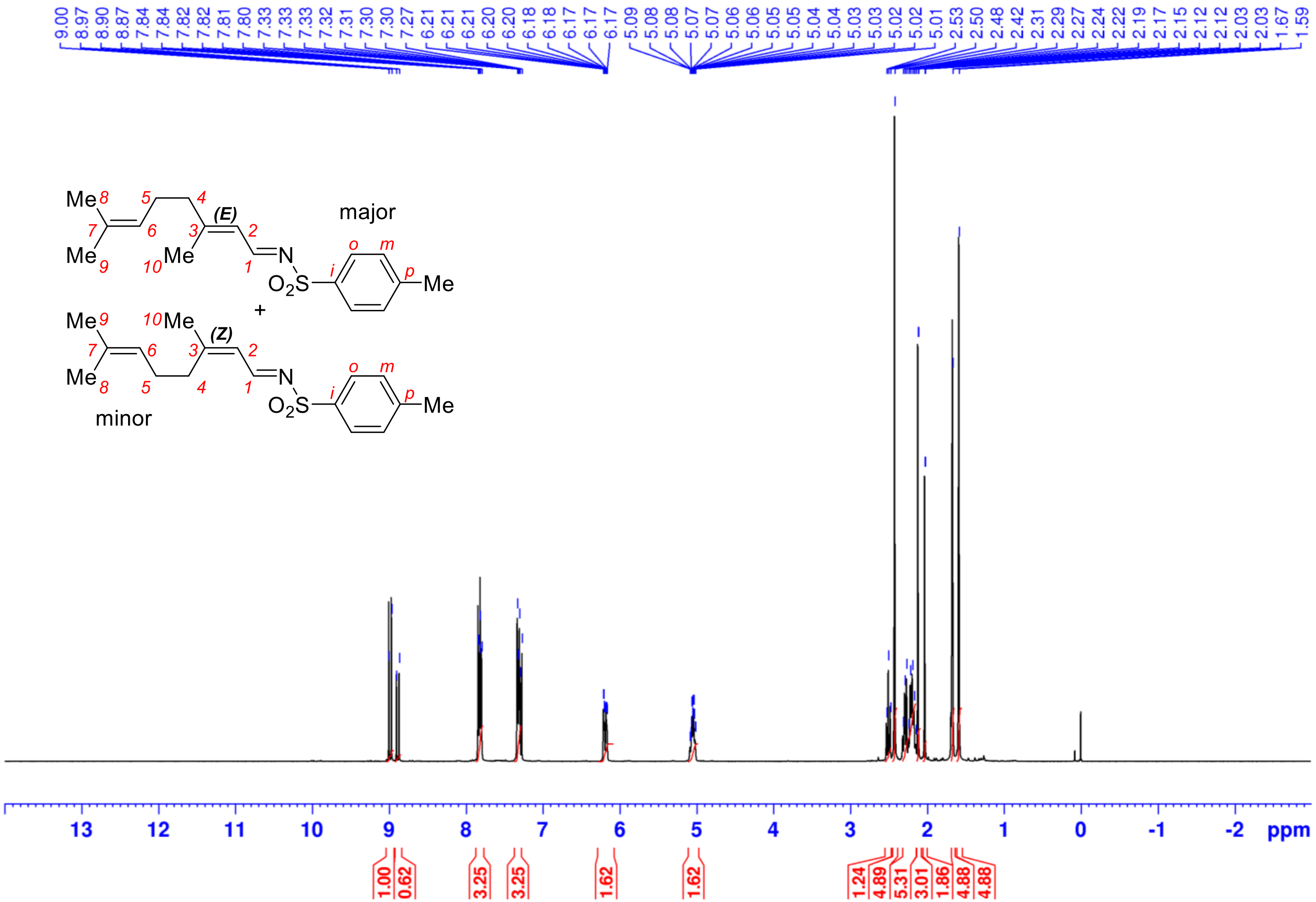
[S3] N. Kaur, P. Singh, P. Banerjee. *Adv. Synth. Catal.* **2021**, *363*, 2813

[S4] D. B. Baudry, A. Dormond, F. Duris, J. M. Bernard, J. R. Desmurs. *J. Fluor. Chem.* **2003**, *121*, 233

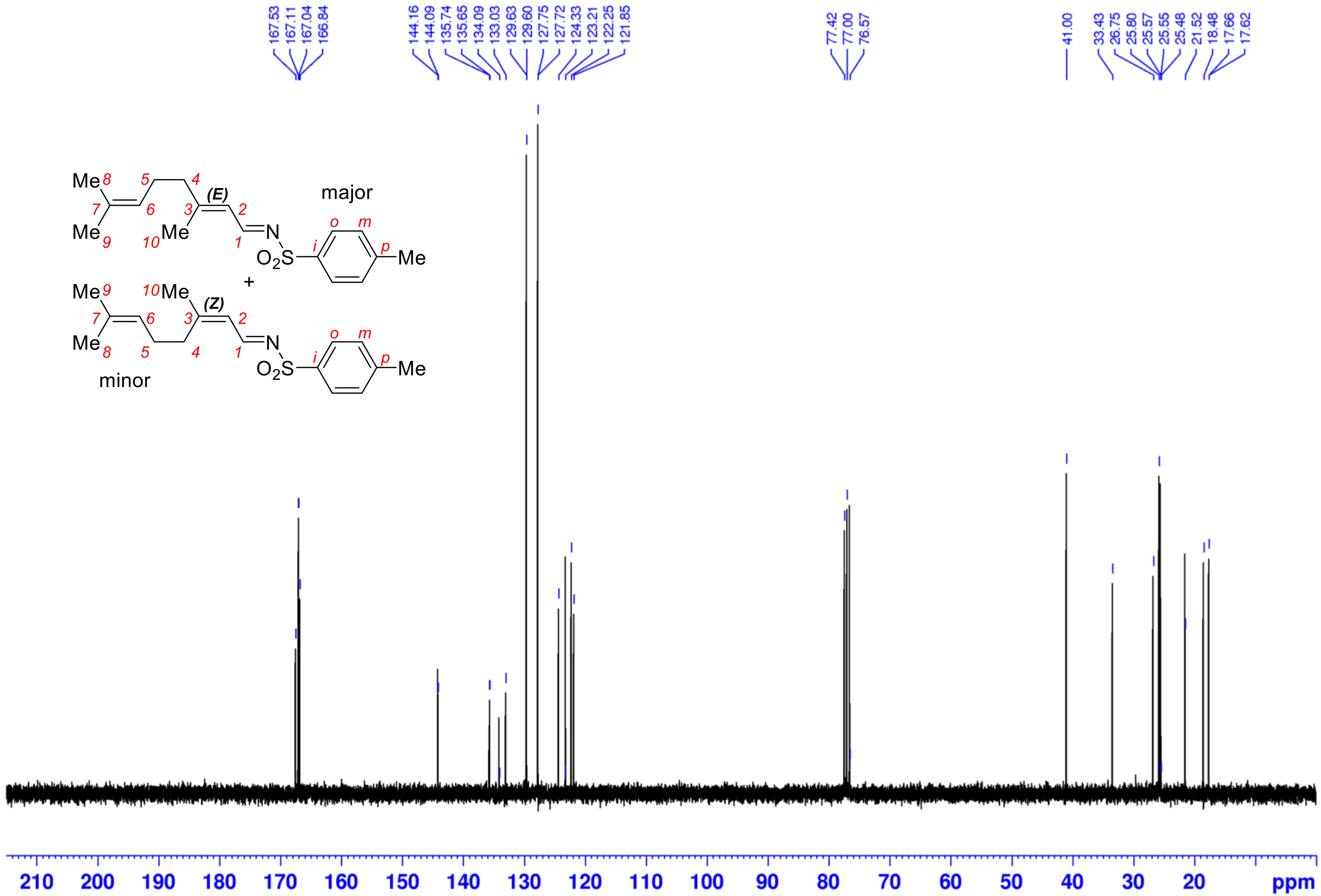
[S5] a) R. A. Novikov, A. V. Tarasova, V. A. Korolev, V. P. Timofeev, Yu. V. Tomilov. *Angew. Chem. Int. Ed.* **2014**, *53*, 3187. b) O. A. Ivanova, E. M. Budynina, A. O. Chagarovskiy, A. E. Kaplun, I. V. Trushkov, M. Ya. Melnikov. *Adv. Synth. Catal.* **2011**, *353*, 1125

[S6] N. S. Radulović, M. M. Tasić, M. Z. Mladenović. *J. Mol. Struct.* **2021**, *1227*, 129427

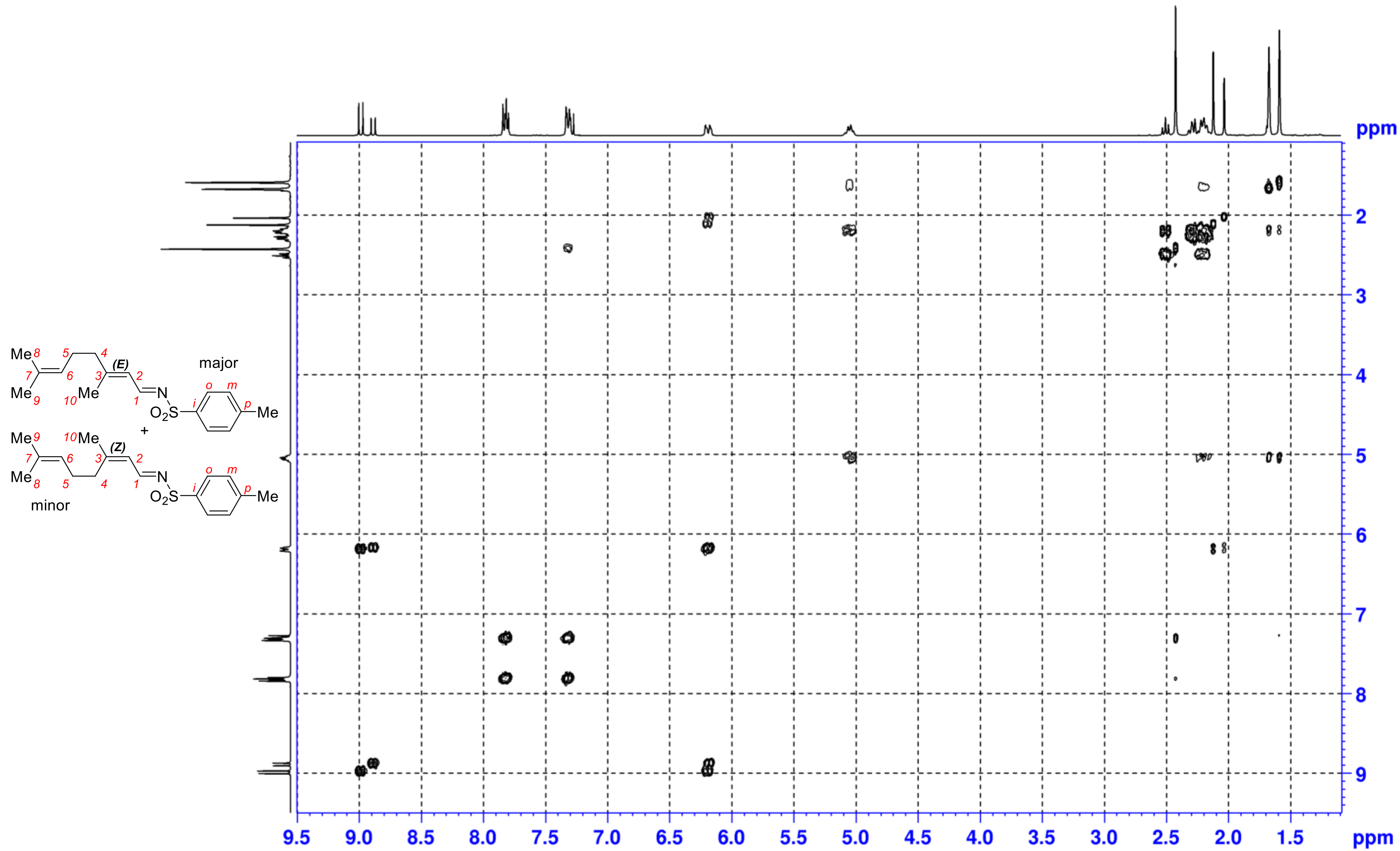
## 15. NMR spectra of new compounds



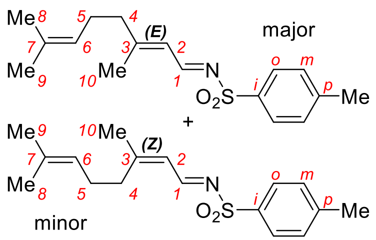

$^1$H NMR spectrum of **2a**, 2*E*/2*Z* 1.6:1 (300.1 MHz, $CDCl_3$)

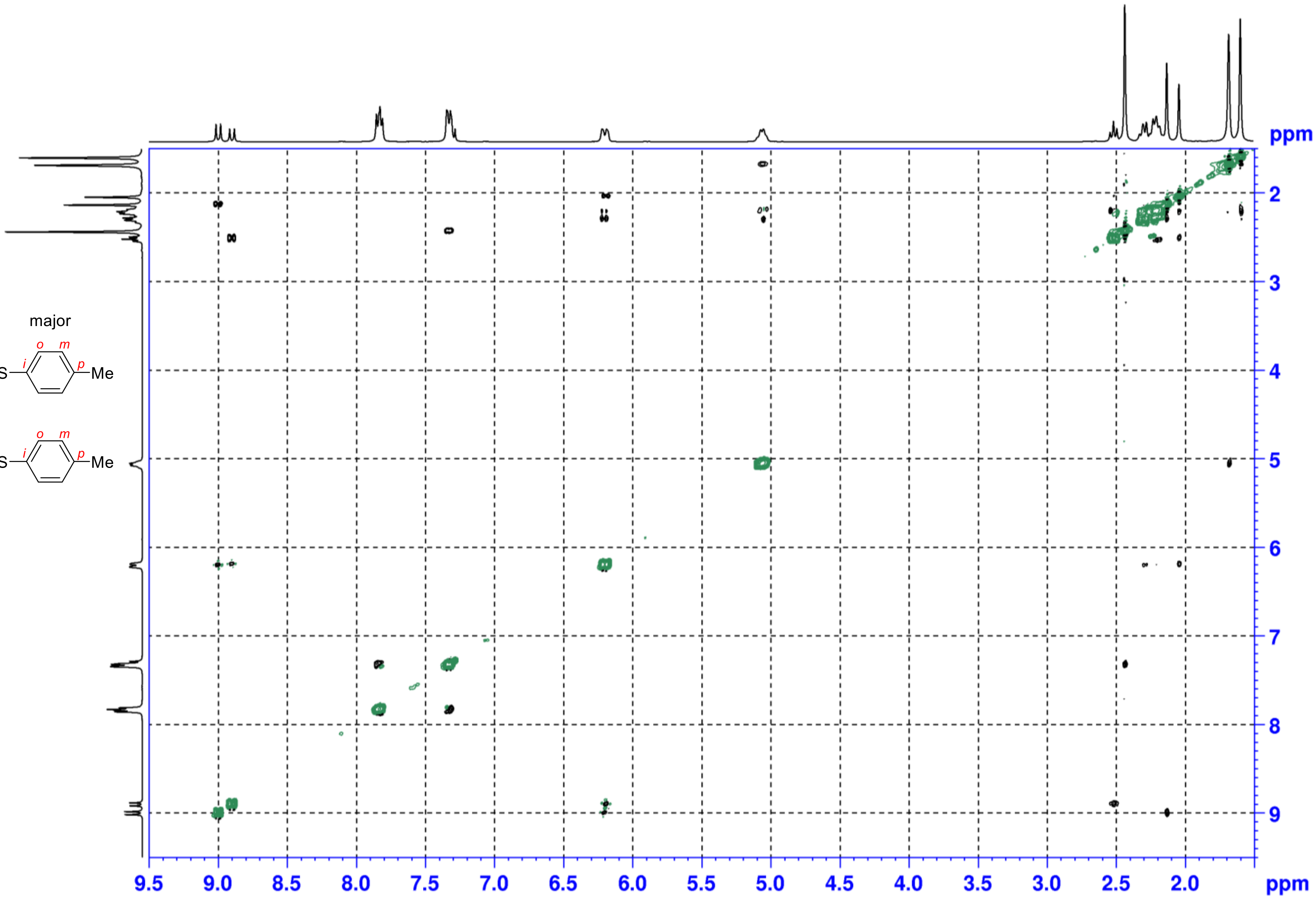



$^{13}$C NMR spectrum of **2a**, 2*E*/2*Z* 1.6:1 (75.5 MHz, $CDCl_3$)

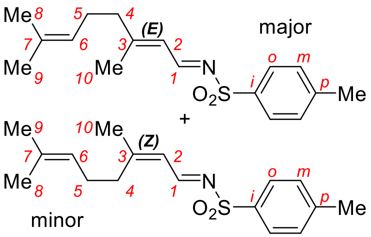


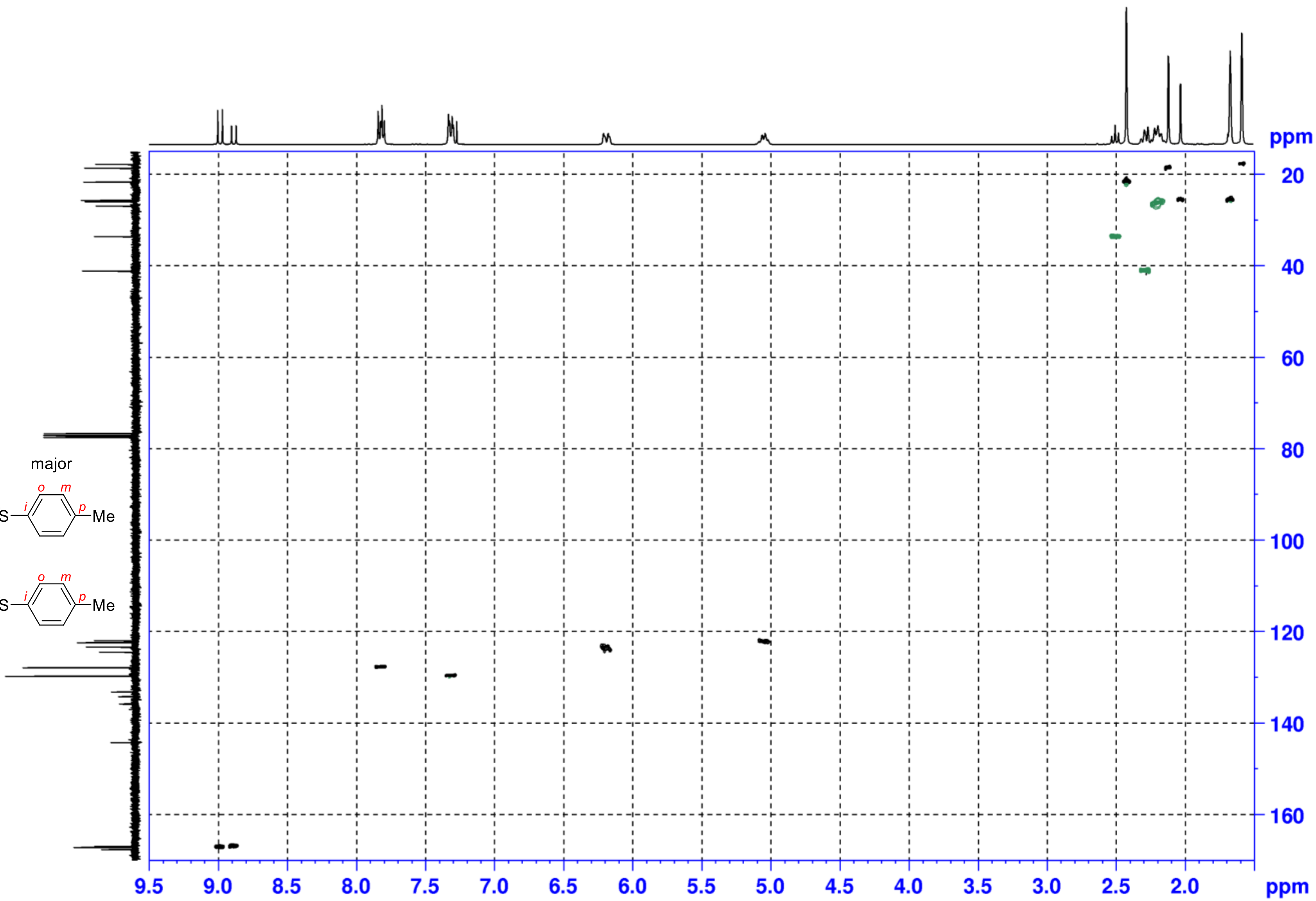

[1]H,[1]H-COSY NMR spectrum of **2a**, 2*E*/2*Z* 1.6:1 (300.1 MHz, $CDCl_3$)



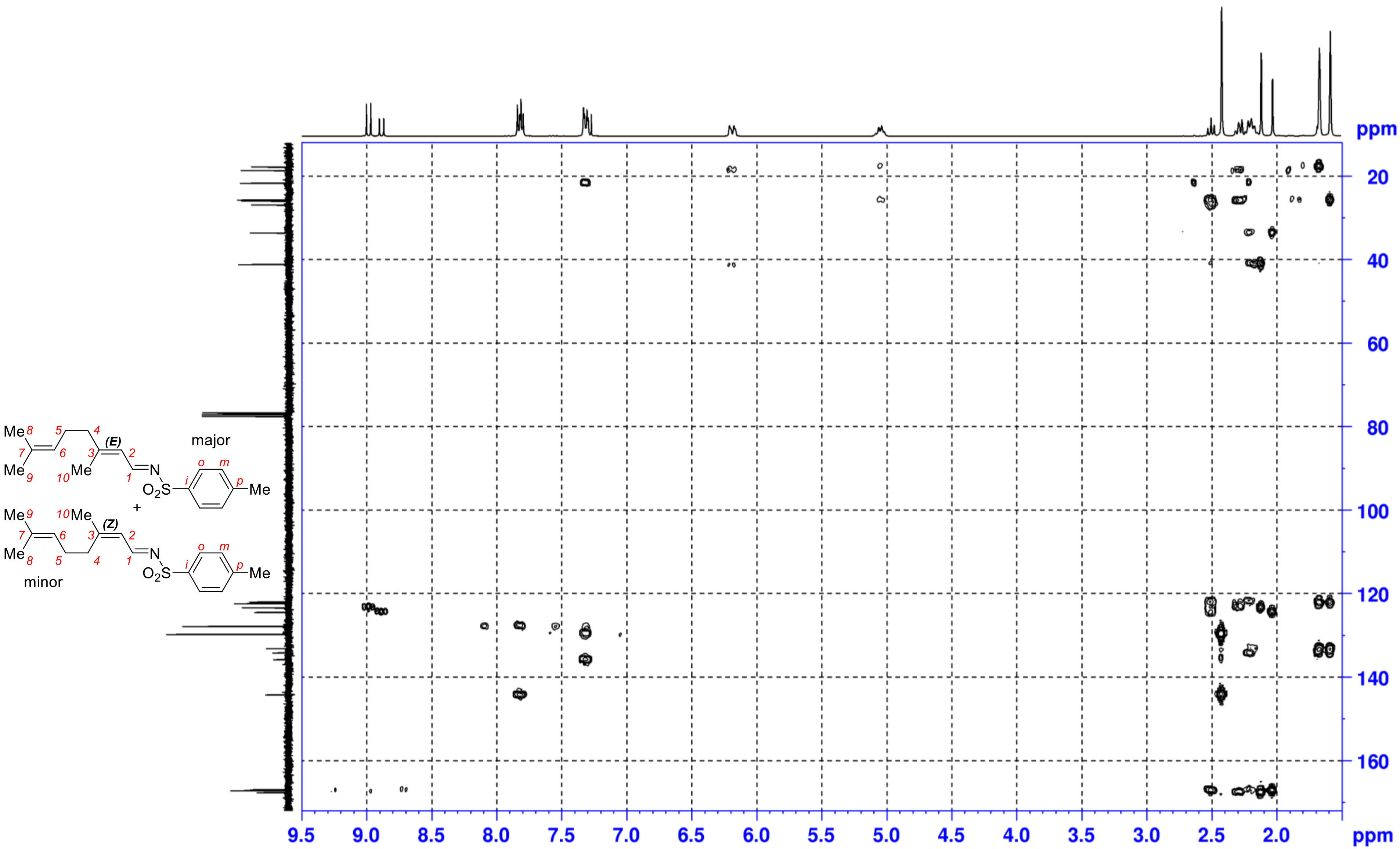



[1]H,[1]H-NOESY NMR spectrum of **2a**, 2*E*/2*Z* 1.6:1 (300.1 MHz, $CDCl_3$)

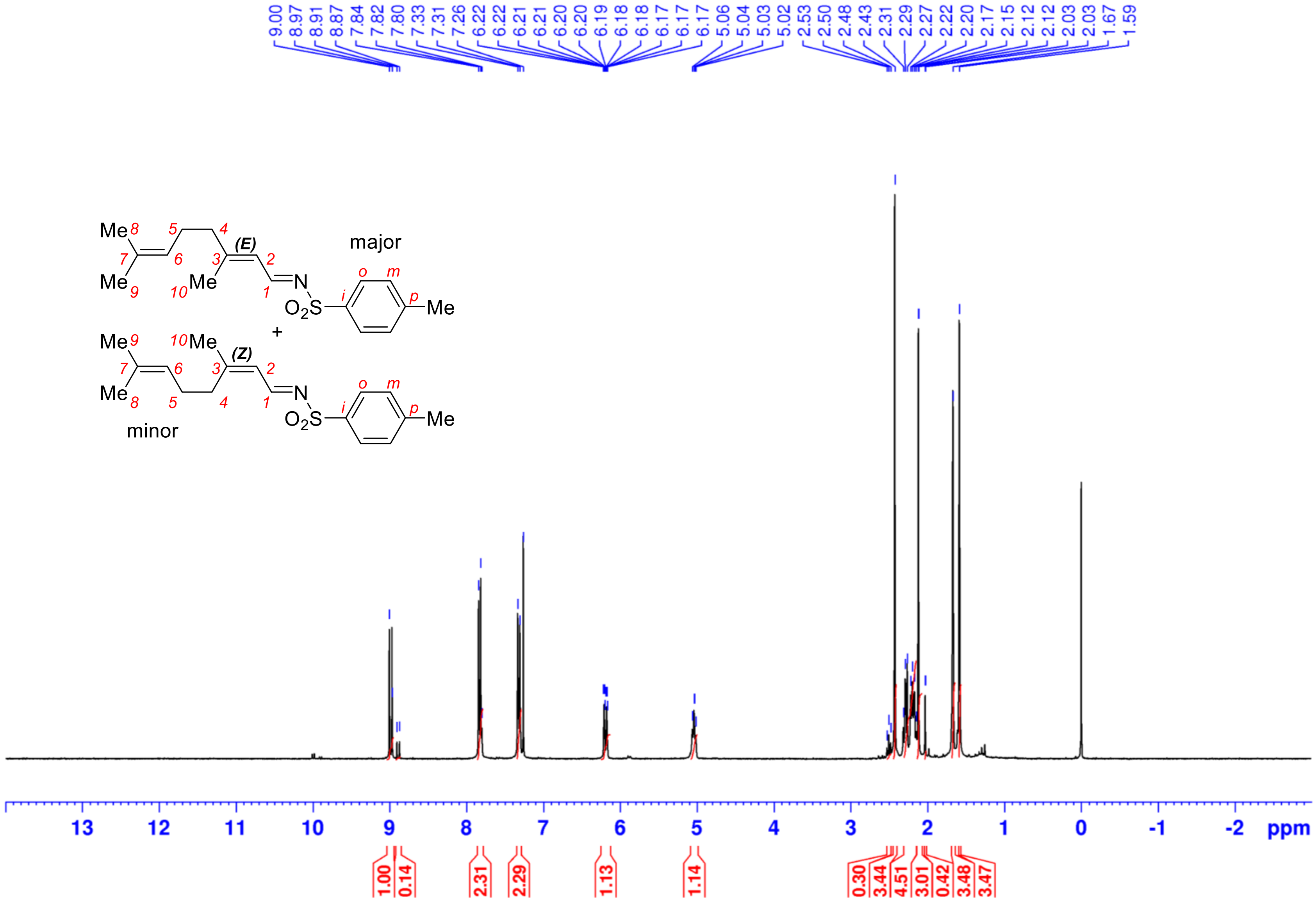


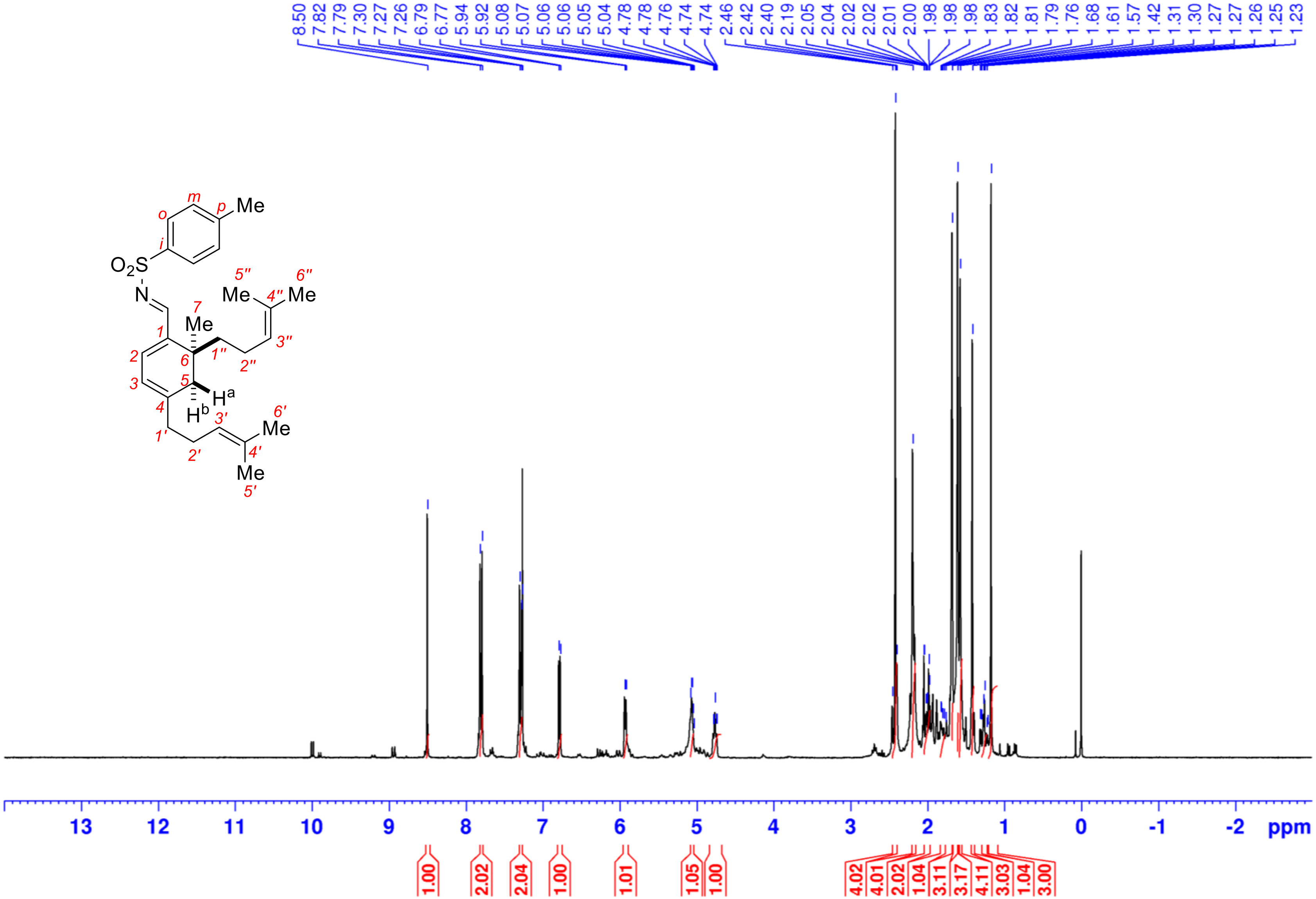

$^{1}H,^{13}C$-edited-HSQC NMR spectrum of **2a**, 2*E*/2*Z* 1.6:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)



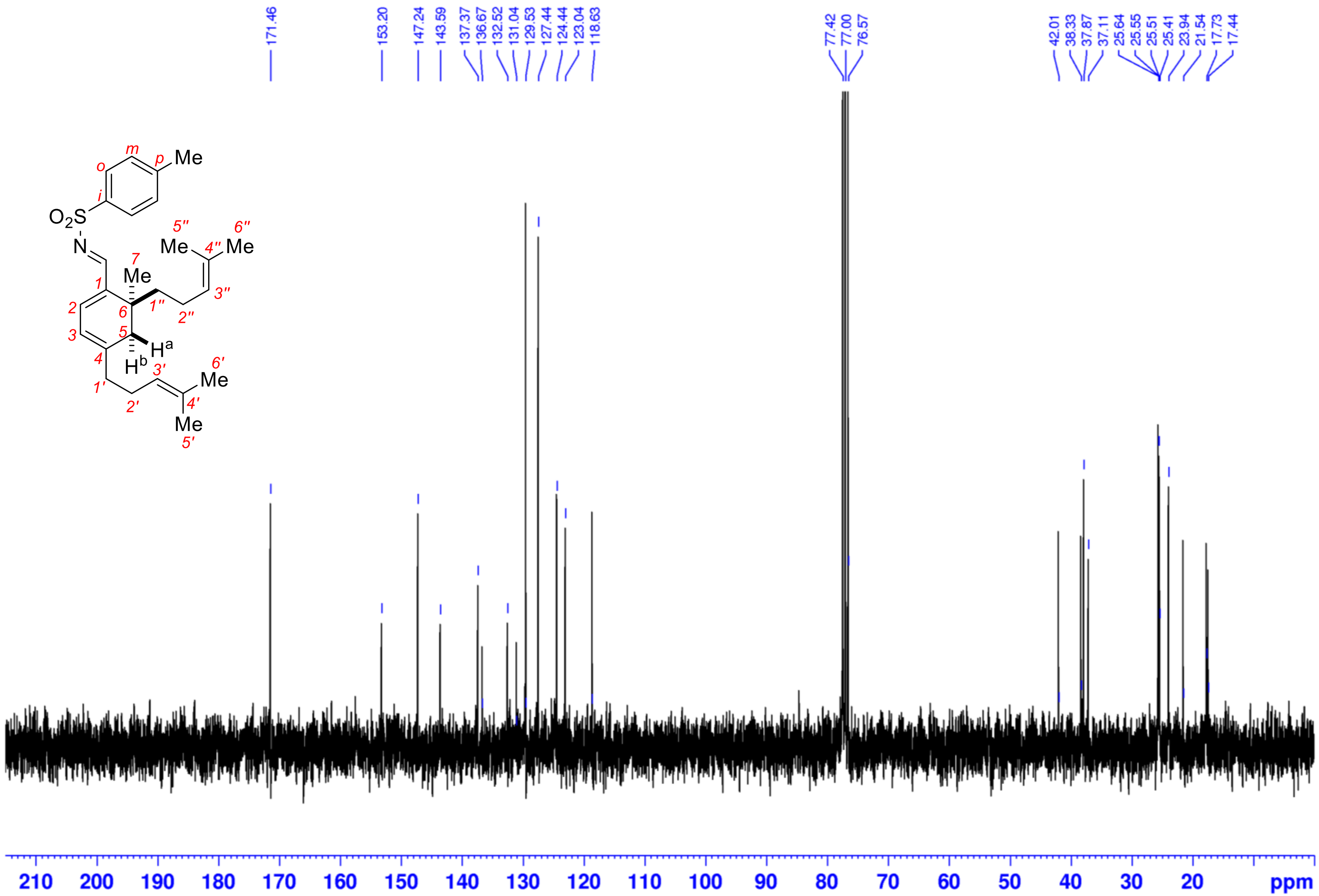

$^{1}H,^{13}C$-HMBC NMR spectrum of **2a**, 2*E*/2*Z* 1.6:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)



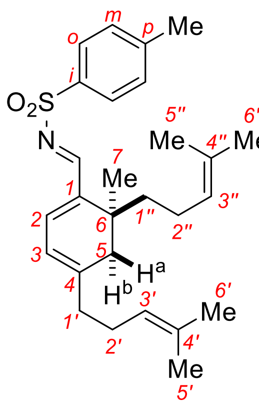

[1]H NMR spectrum of **2a**, 2*E*/2*Z* 7:1 (300.1 MHz, $CDCl_3$)

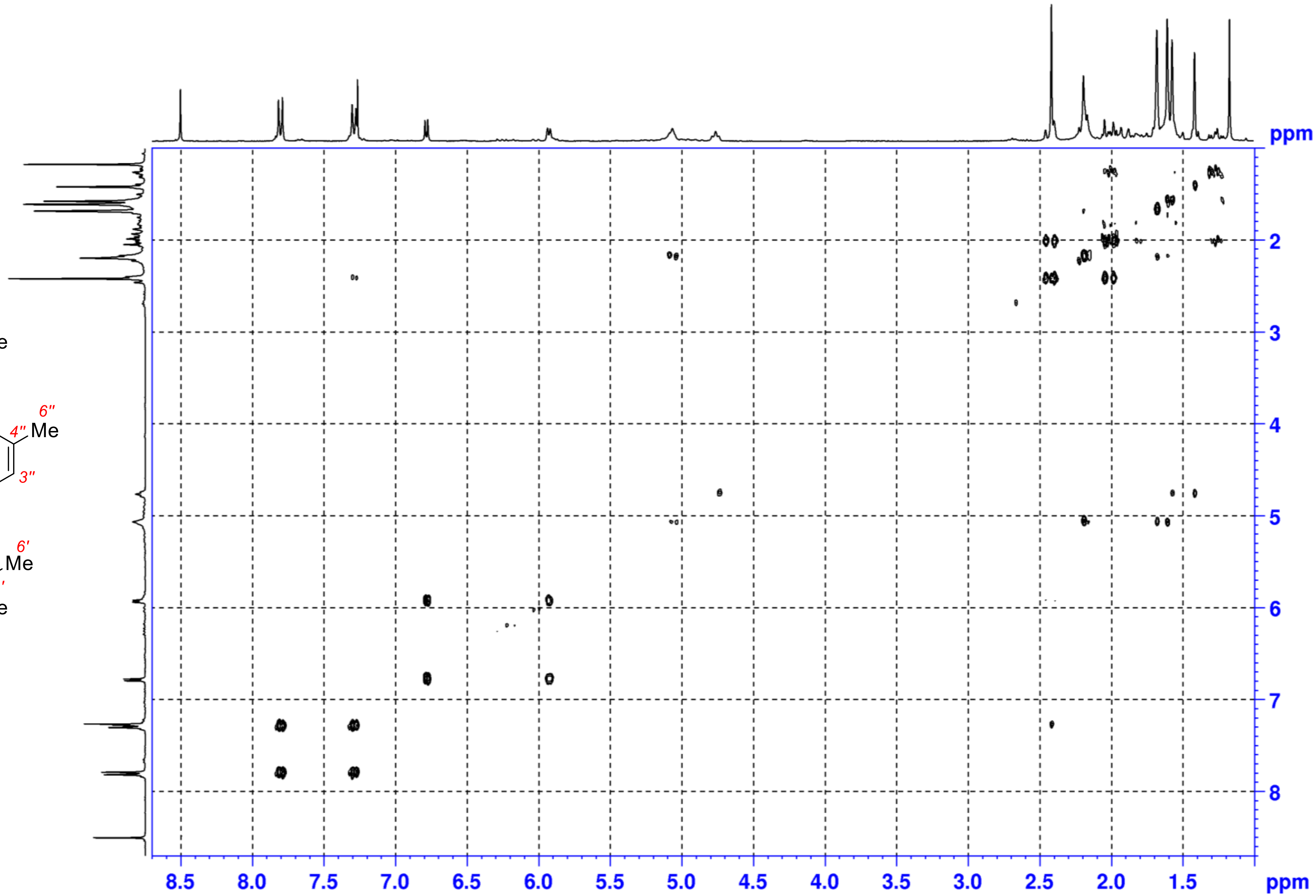



$^1$H NMR spectrum of **S1** (300.1 MHz, $CDCl_3$)

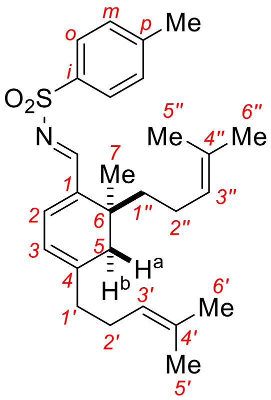


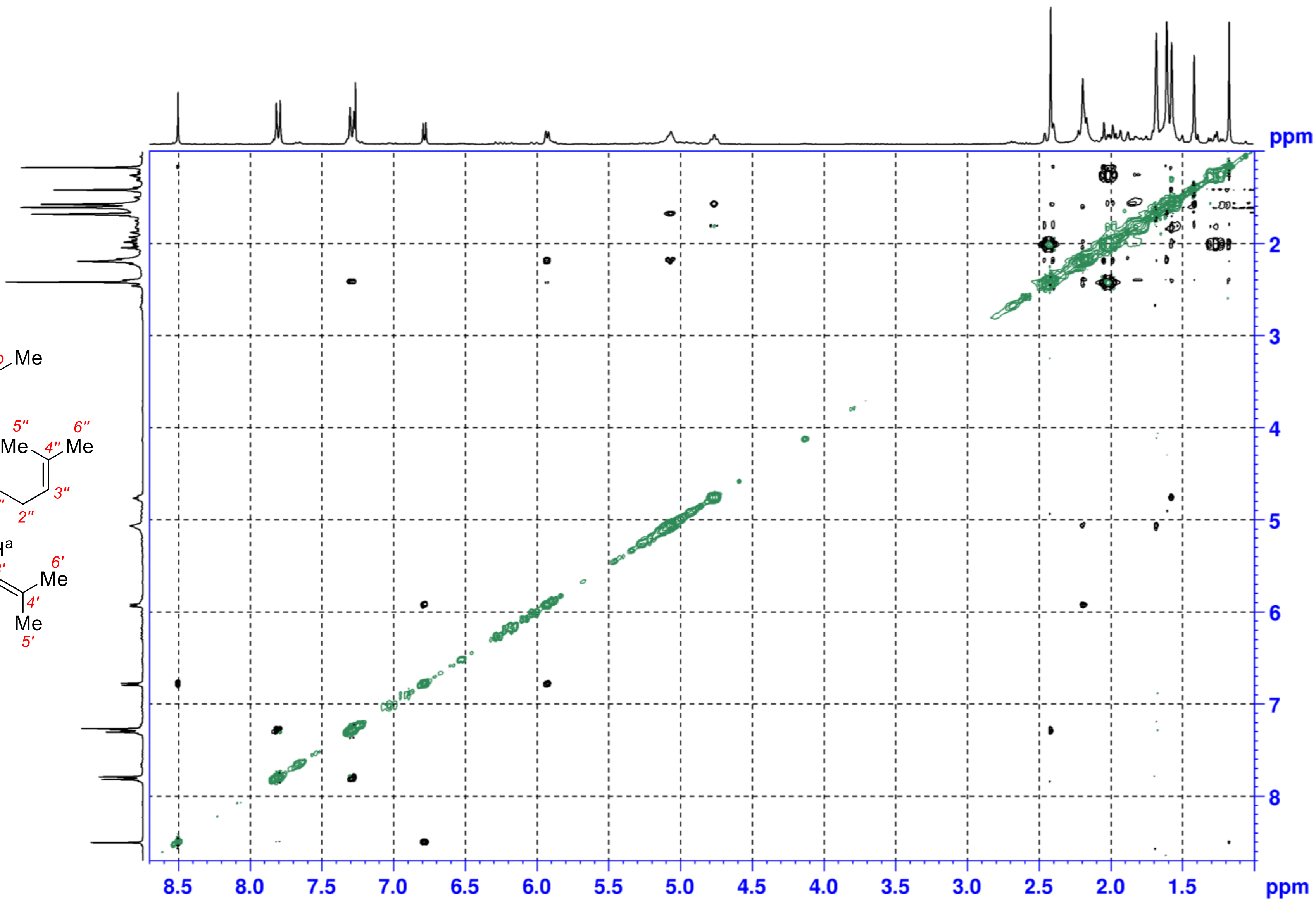

$^{13}$C NMR spectrum of **S1** (75.5 MHz, $CDCl_3$)



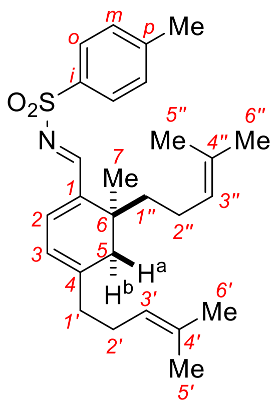



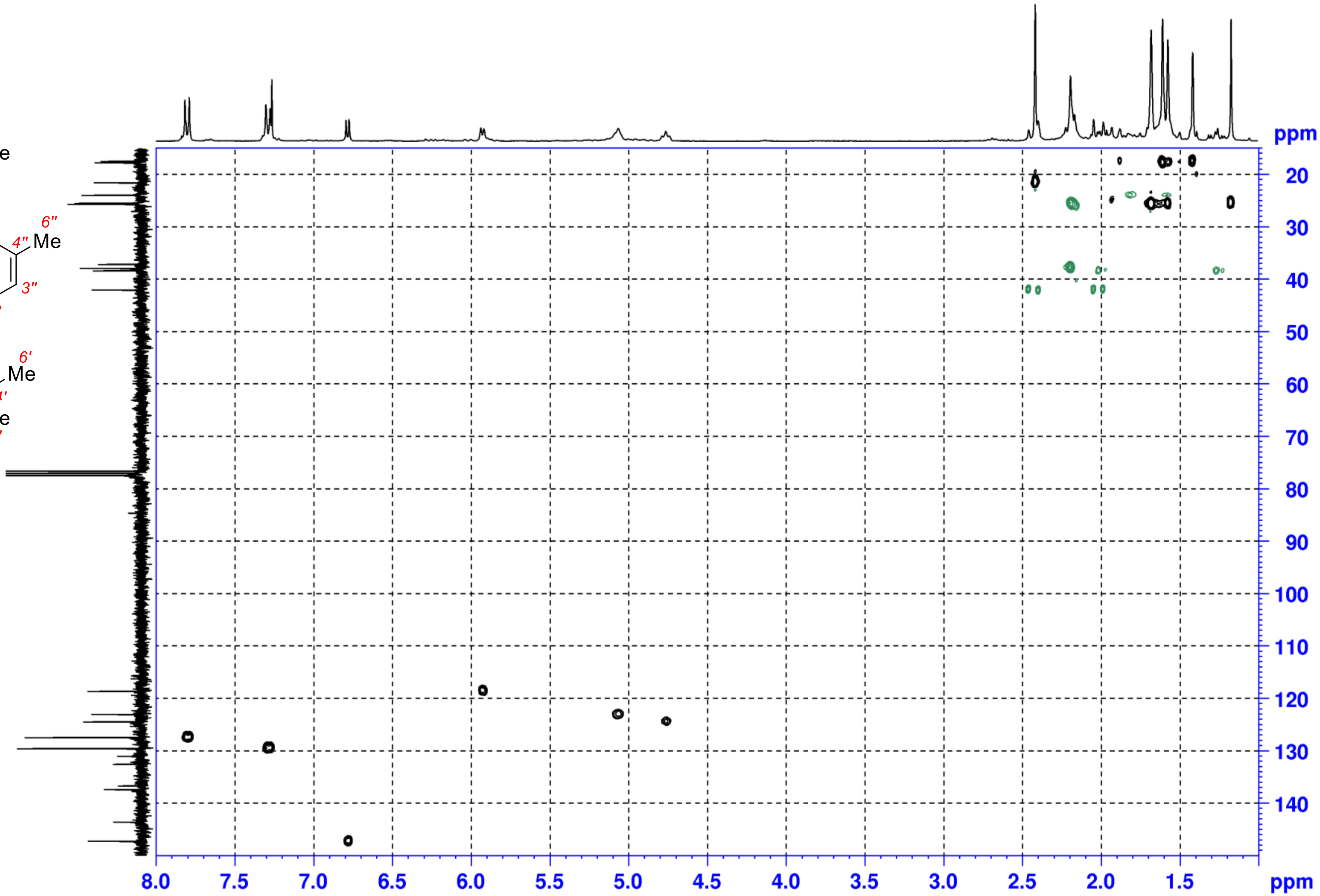

$^1H,^1H$-COSY NMR spectrum of **S1** (300.1 MHz, $CDCl_3$)



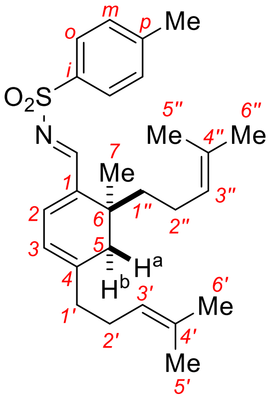


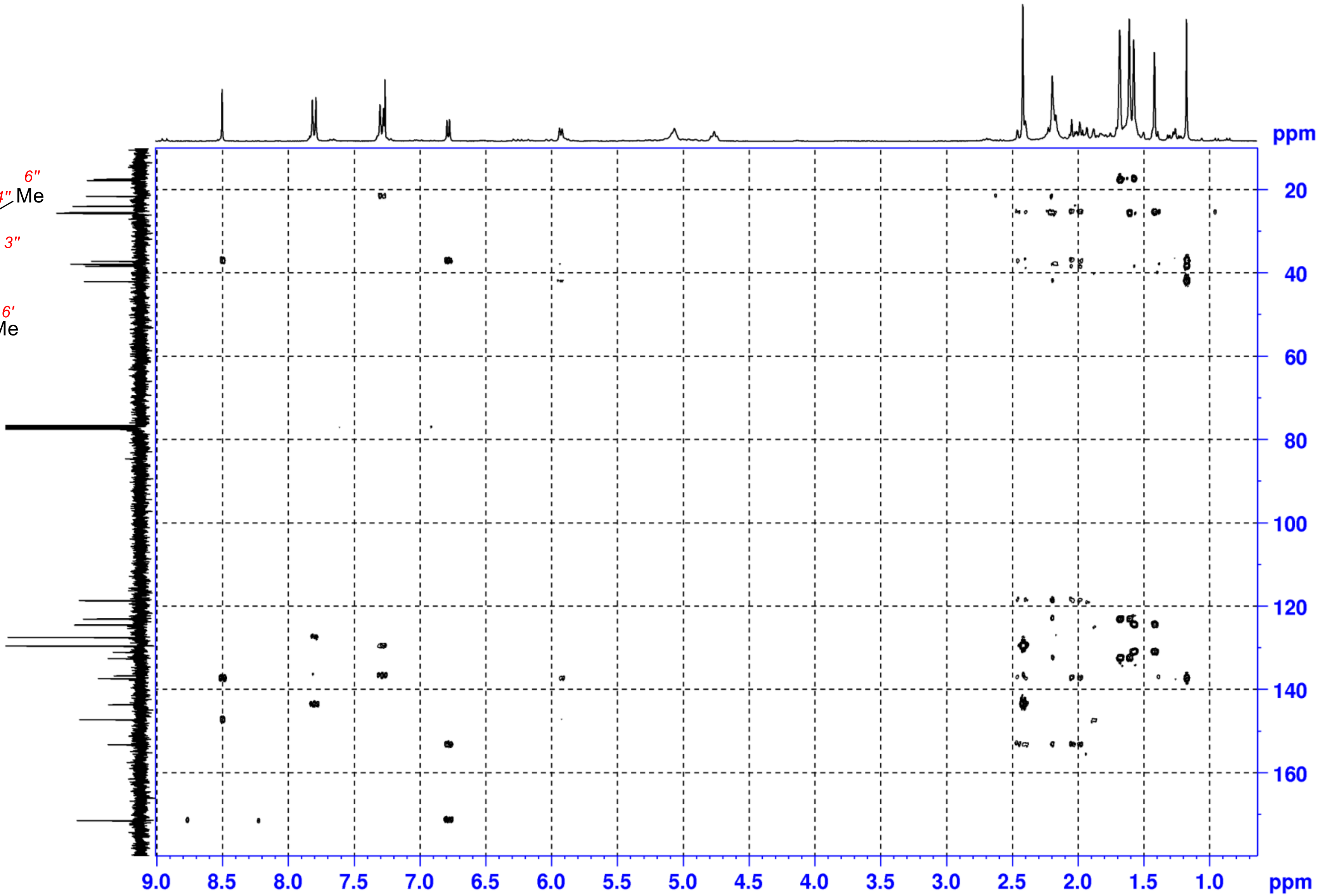

$^{1}H,^{1}H$-NOESY NMR spectrum of **S1** (300.1 MHz, $CDCl_3$)



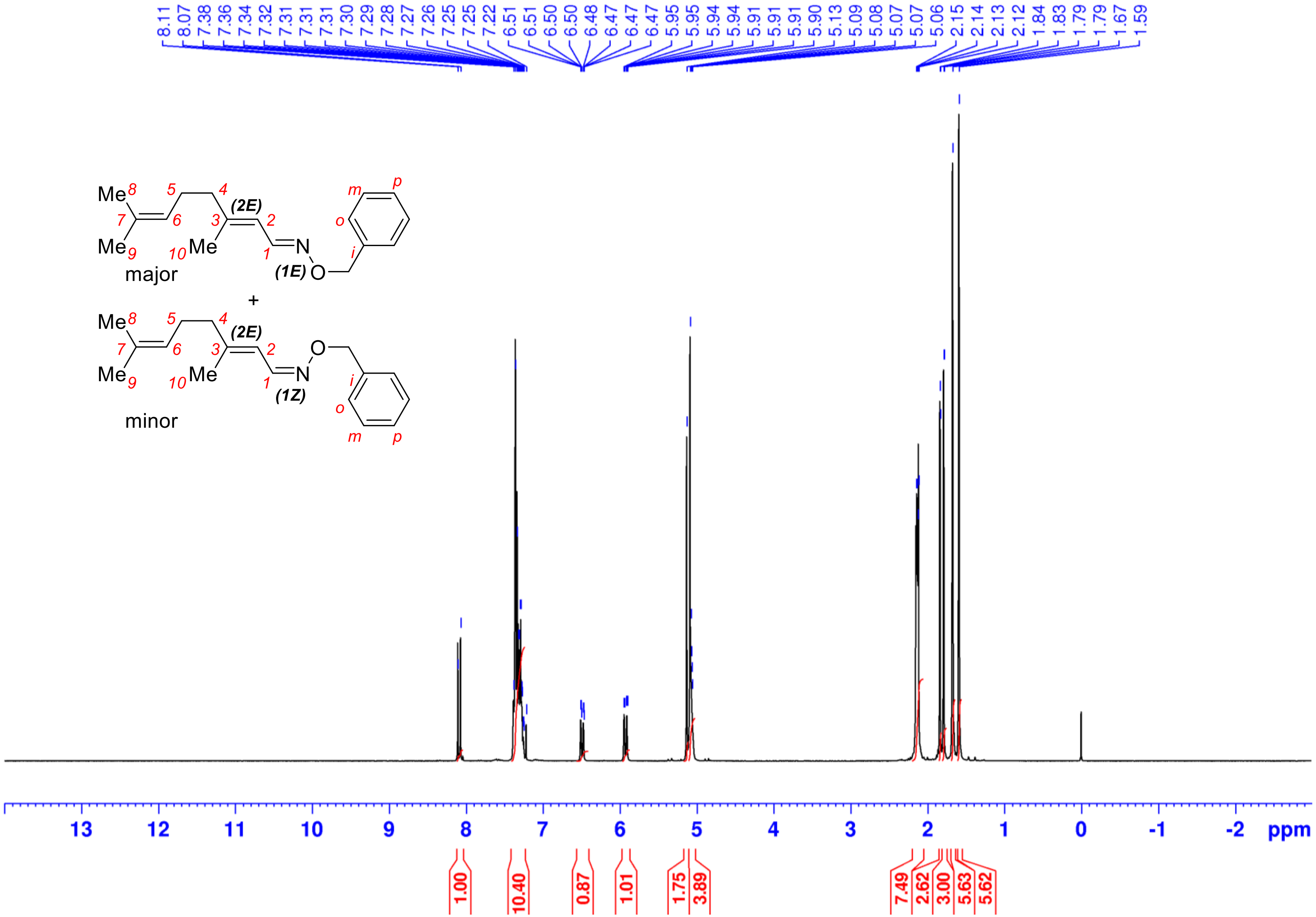




$^{1}H,^{13}C$-edited-HSQC NMR spectrum of **S1** ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

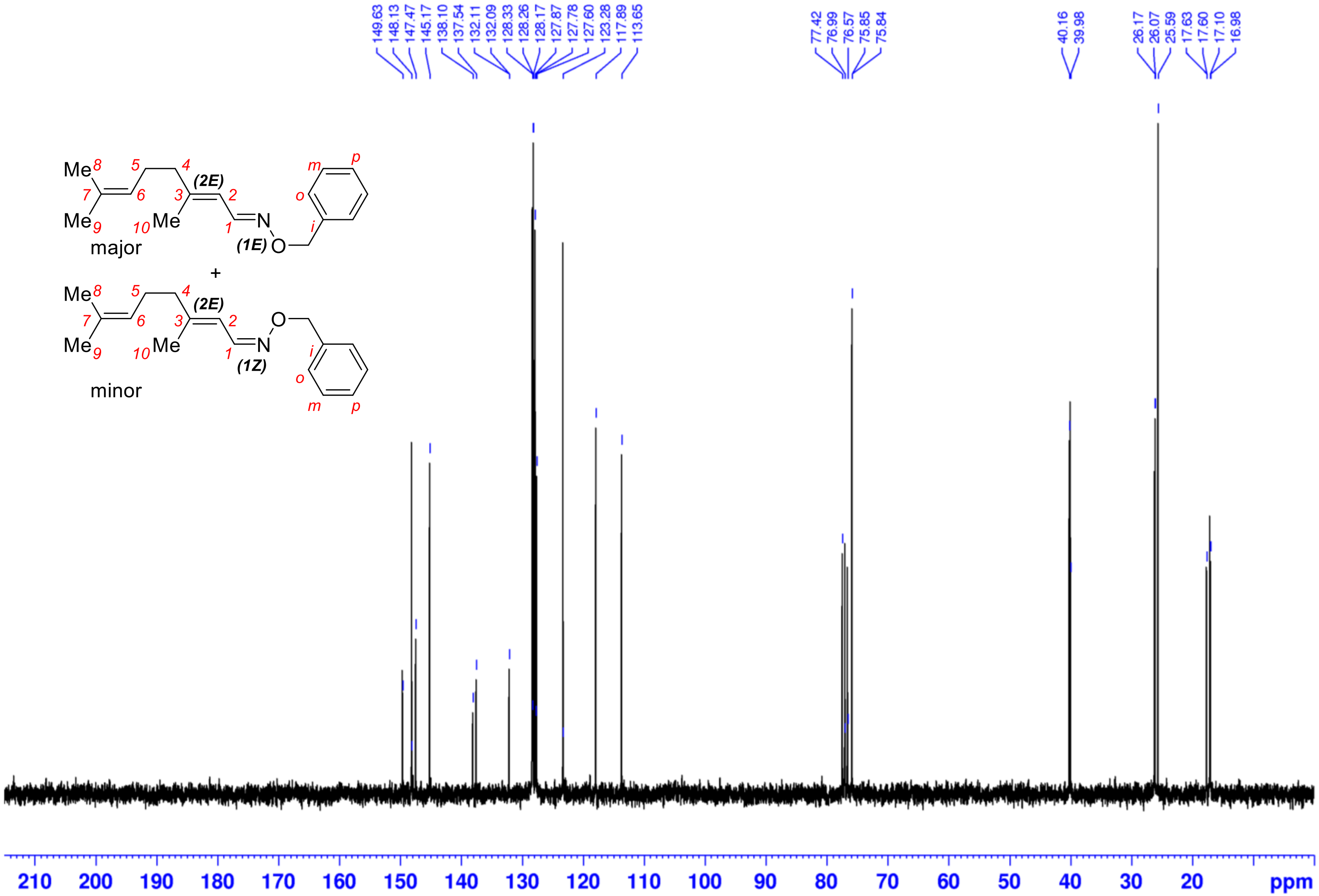


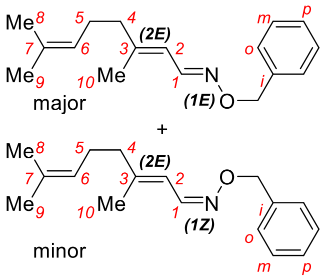

$^1$H,$^{13}$C-HMBC NMR spectrum of **S1** ($^1$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)

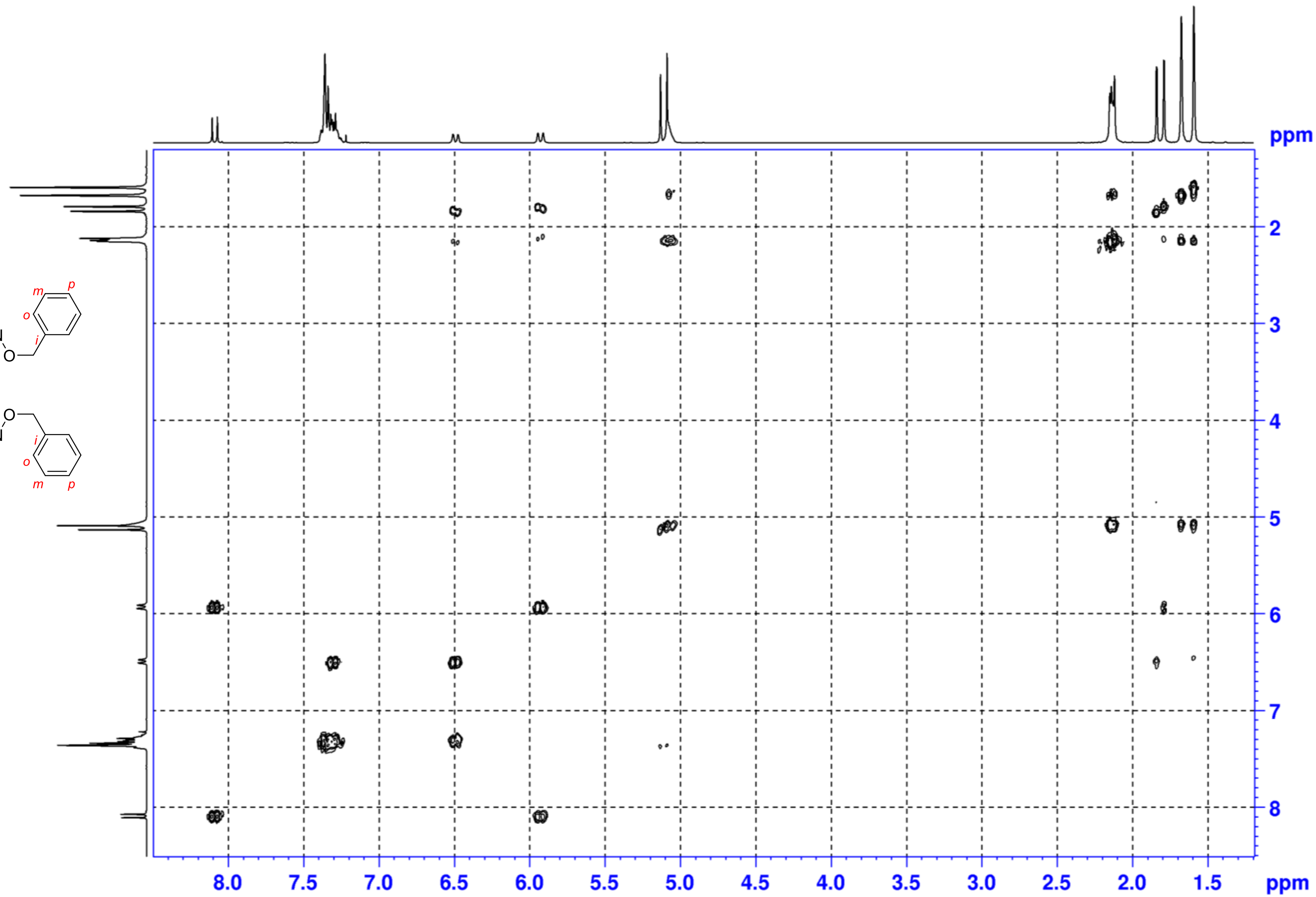



[1]H NMR spectrum of 2*E*-**2c**, 1*E*/1*Z* 1.2:1 (300.1 MHz, $CDCl_3$)

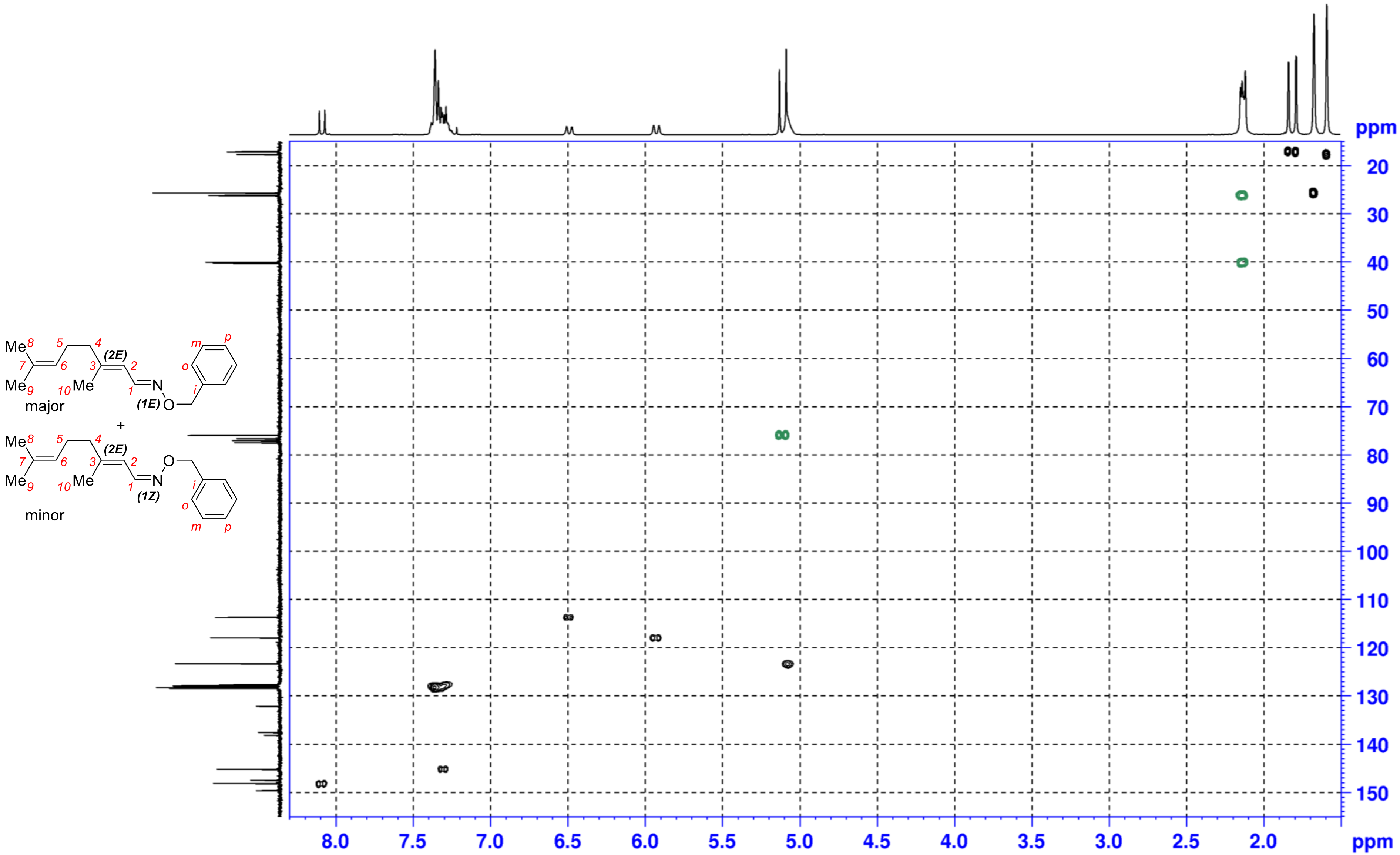



[13]C NMR spectrum of 2*E*-**2c**, 1*E*/1*Z* 1.2:1 (75.5 MHz, $CDCl_3$)

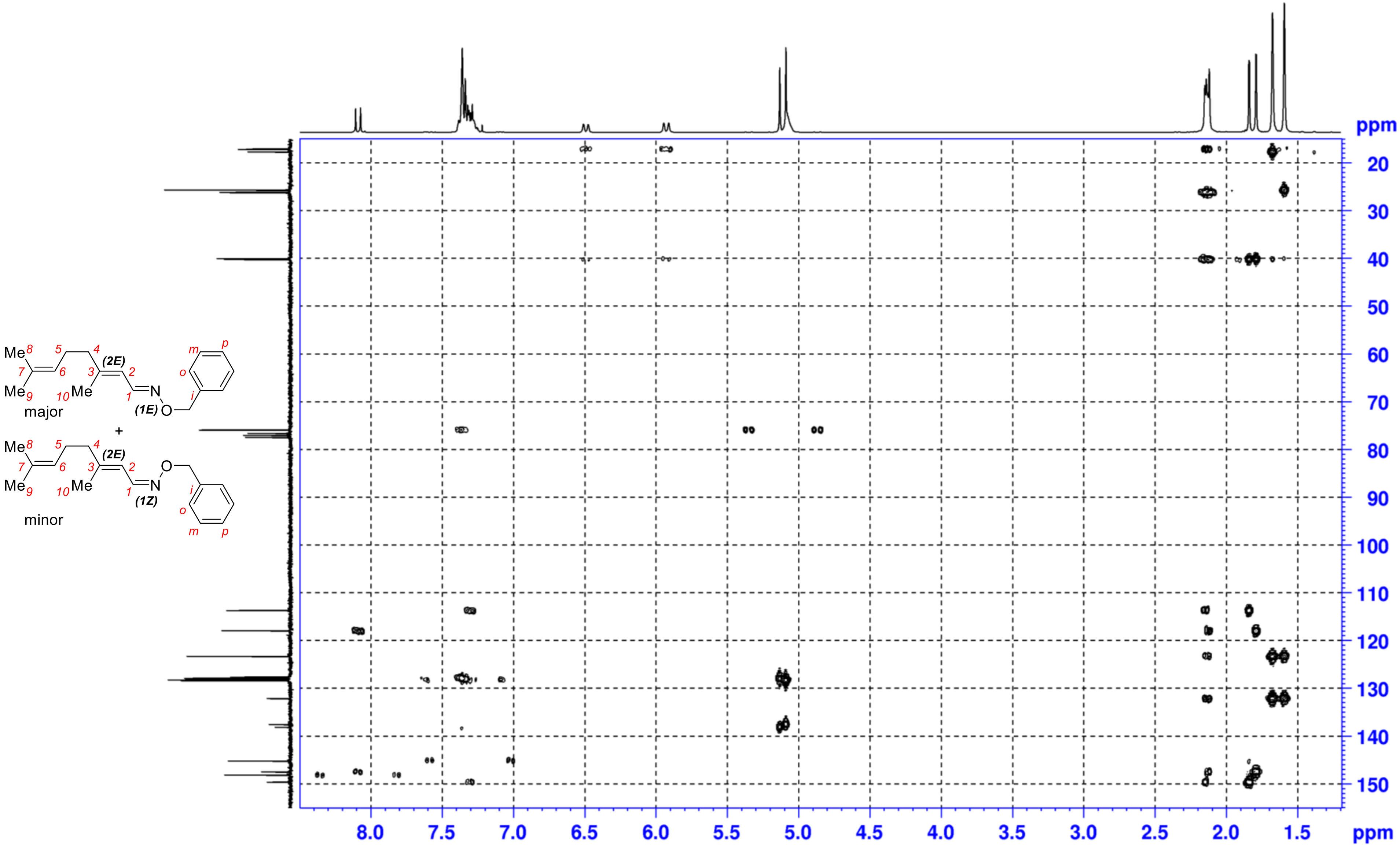


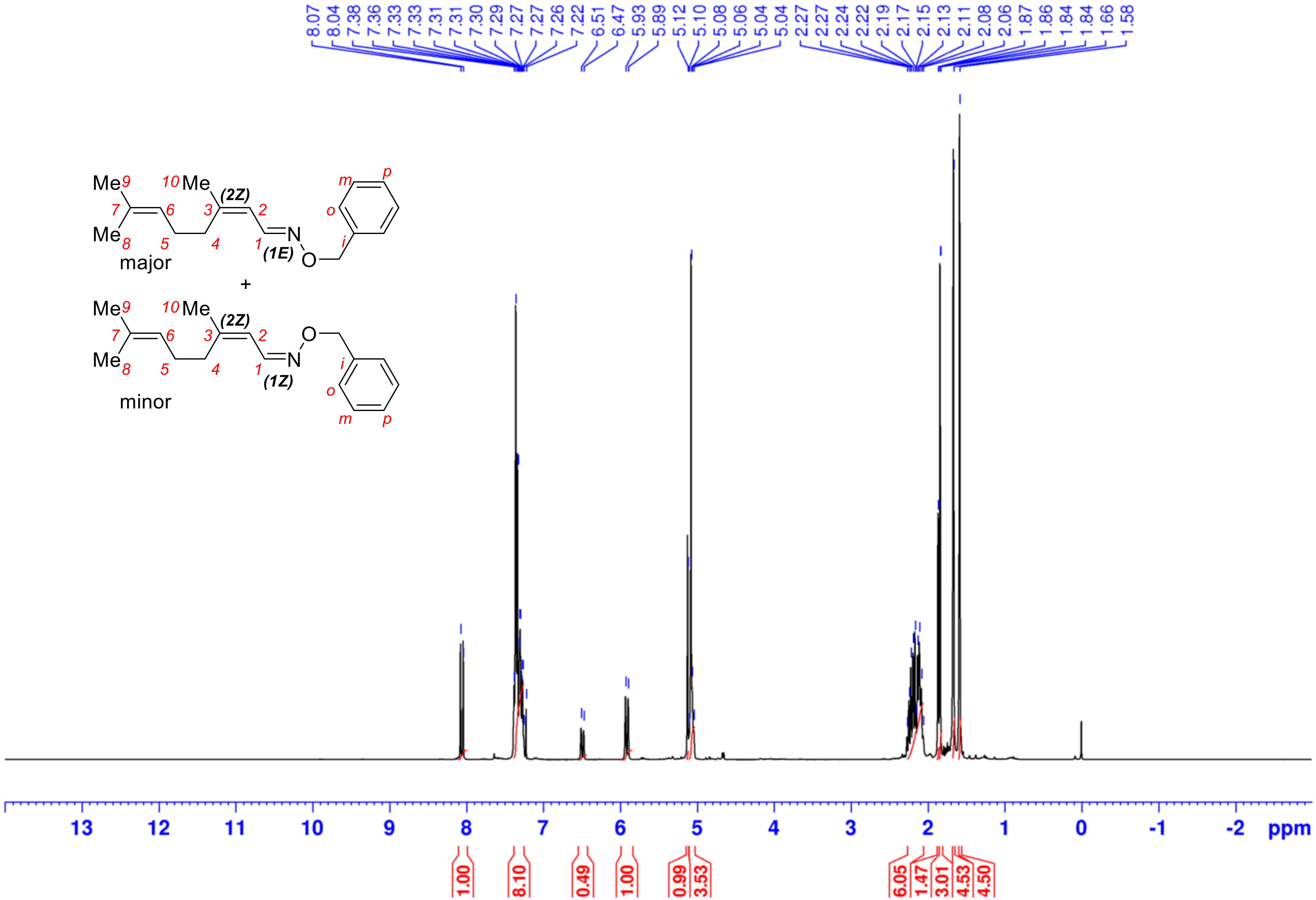

$^1$H,$^1$H-COSY NMR spectrum of 2*E*-**2c**, 1*E*/1*Z* 1.2:1 (300.1 MHz, $CDCl_3$)



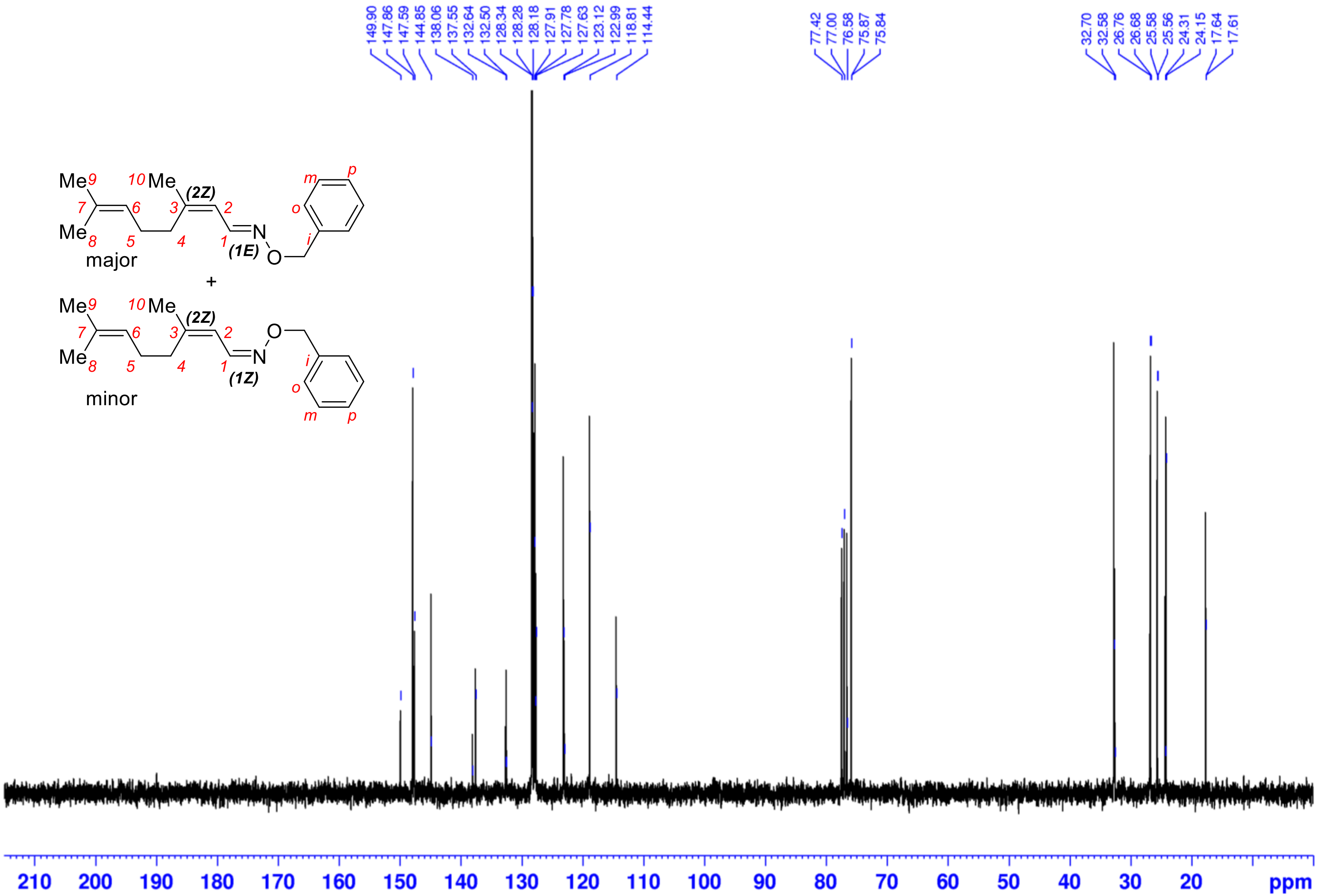

[1]H,[13]C-edited-HSQC NMR spectrum of 2*E*-**2c**, 1*E*/1*Z* 1.2:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)



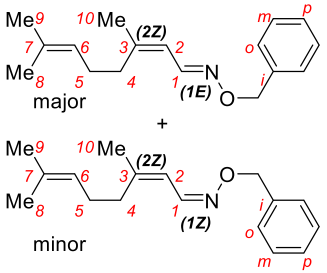

[1]H,[13]C-HMBC NMR spectrum of 2*E*-**2c**, 1*E*/1*Z* 1.2:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

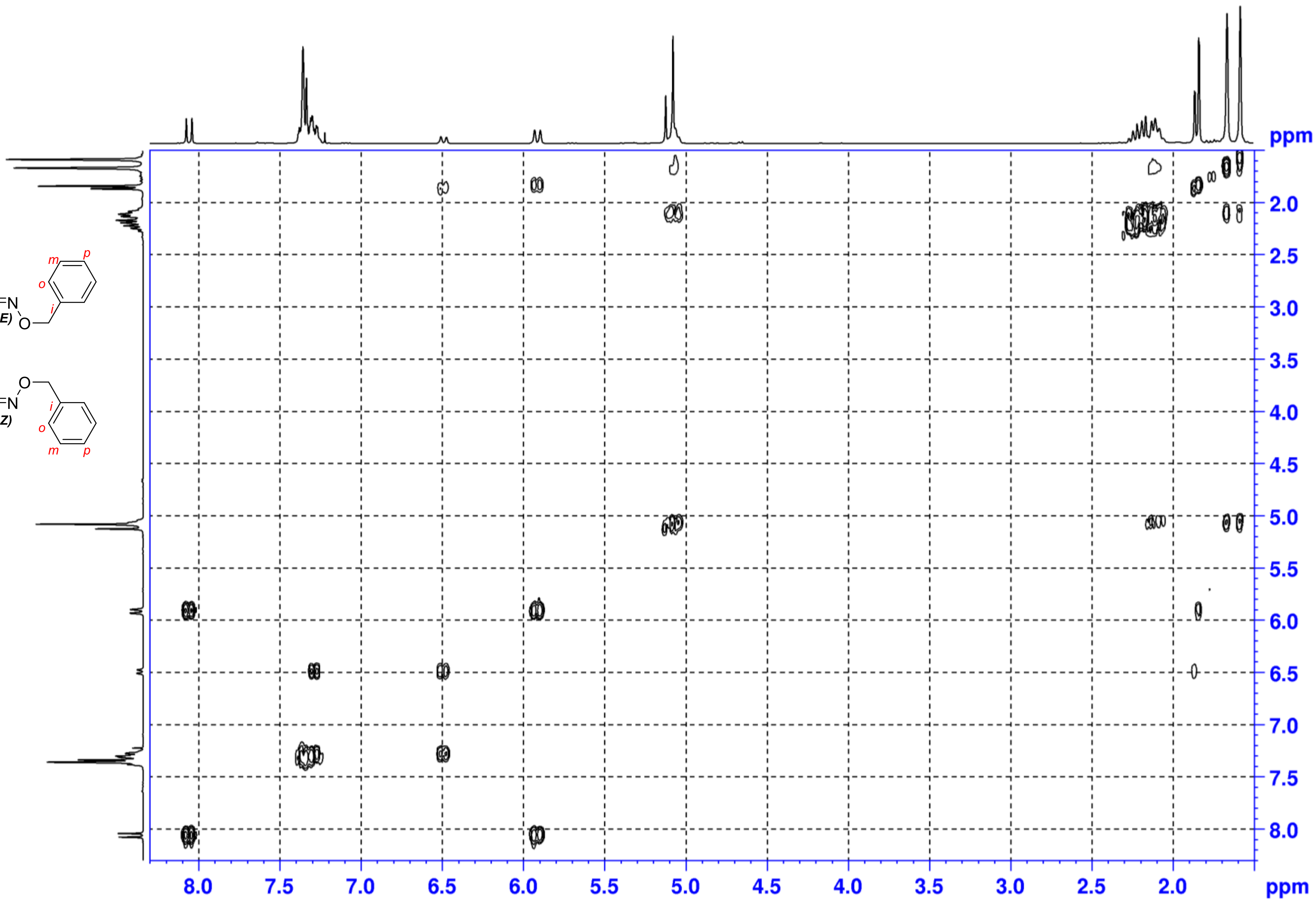



[1]H NMR spectrum of 2*Z*-**2c**, 1*E*/1*Z* 2:1 (300.1 MHz, $CDCl_3$)

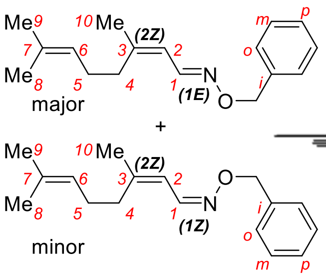


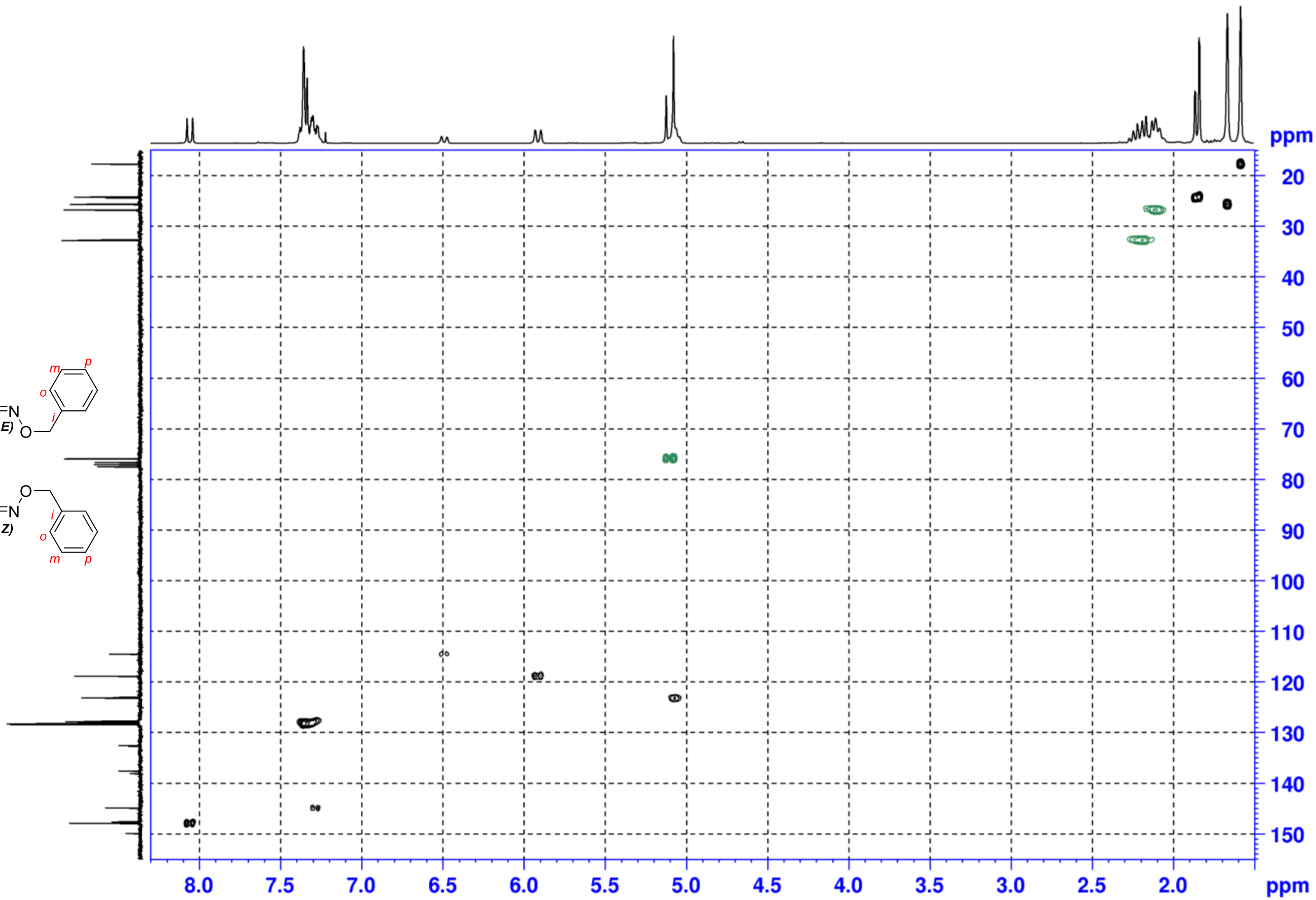

$^{13}$C NMR spectrum of 2*Z*-**2c**, 1*E*/1*Z* 2:1 (75.5 MHz, $CDCl_3$)



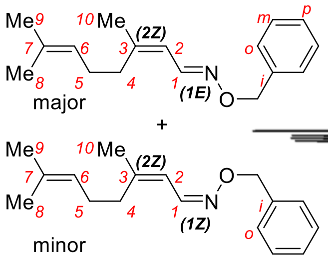



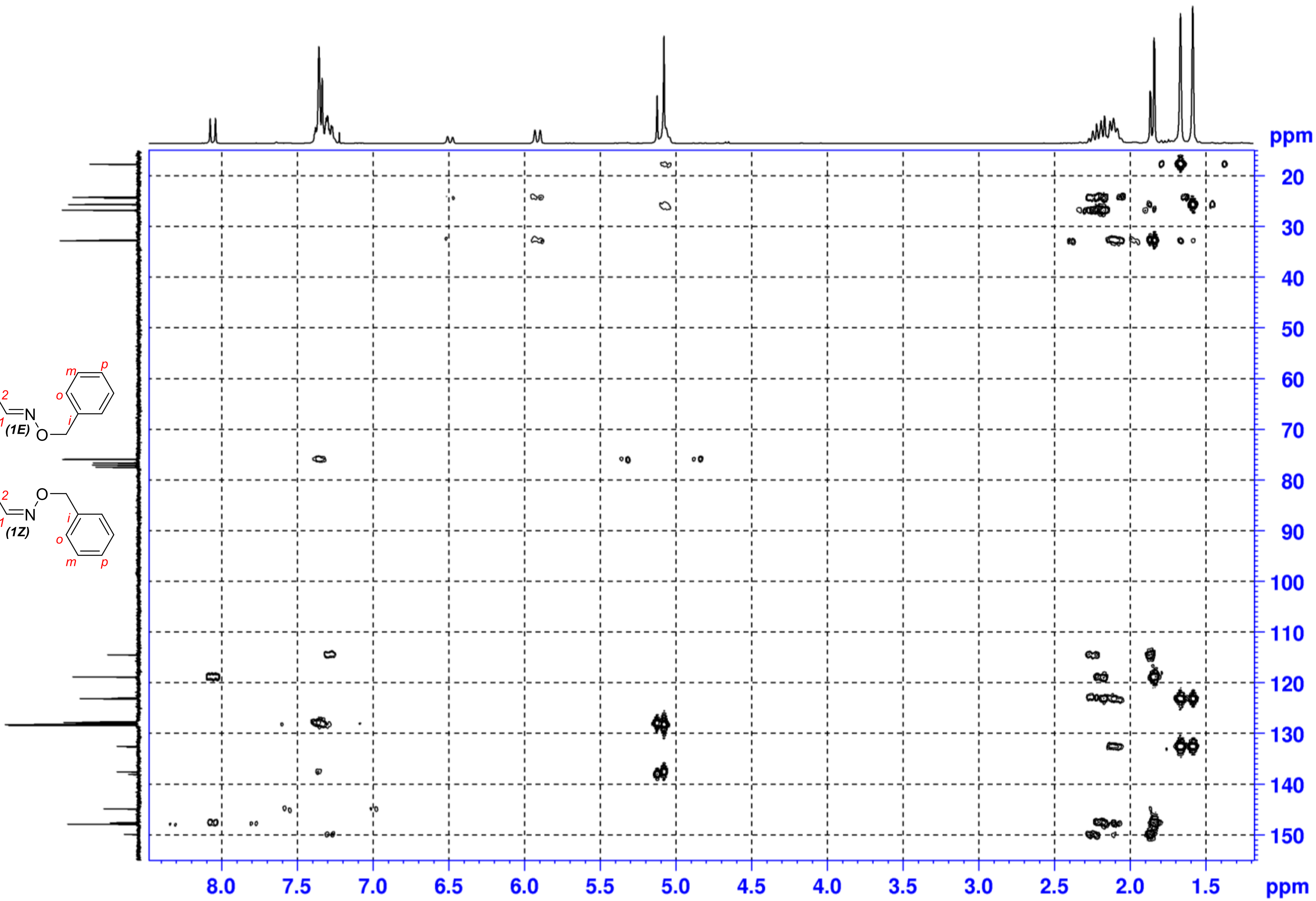
$^{1}H,^{1}H$-COSY NMR spectrum of 2*Z*-**2c**, 1*E*/1*Z* 2:1 (300.1 MHz, $CDCl_3$)



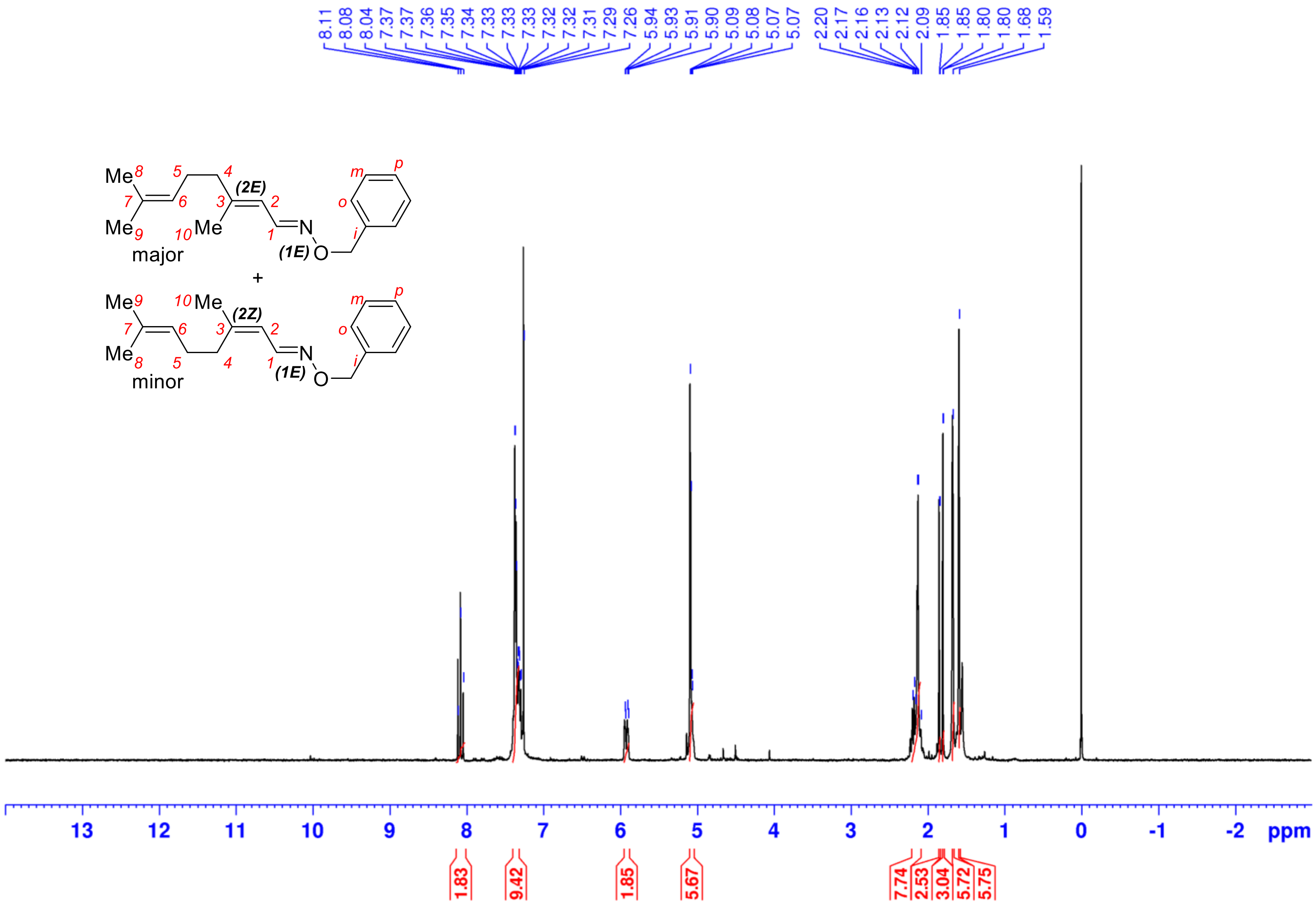




[1]H,[13]C-edited-HSQC NMR spectrum of 2*Z*-**2c**, 1*E*/1*Z* 2:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

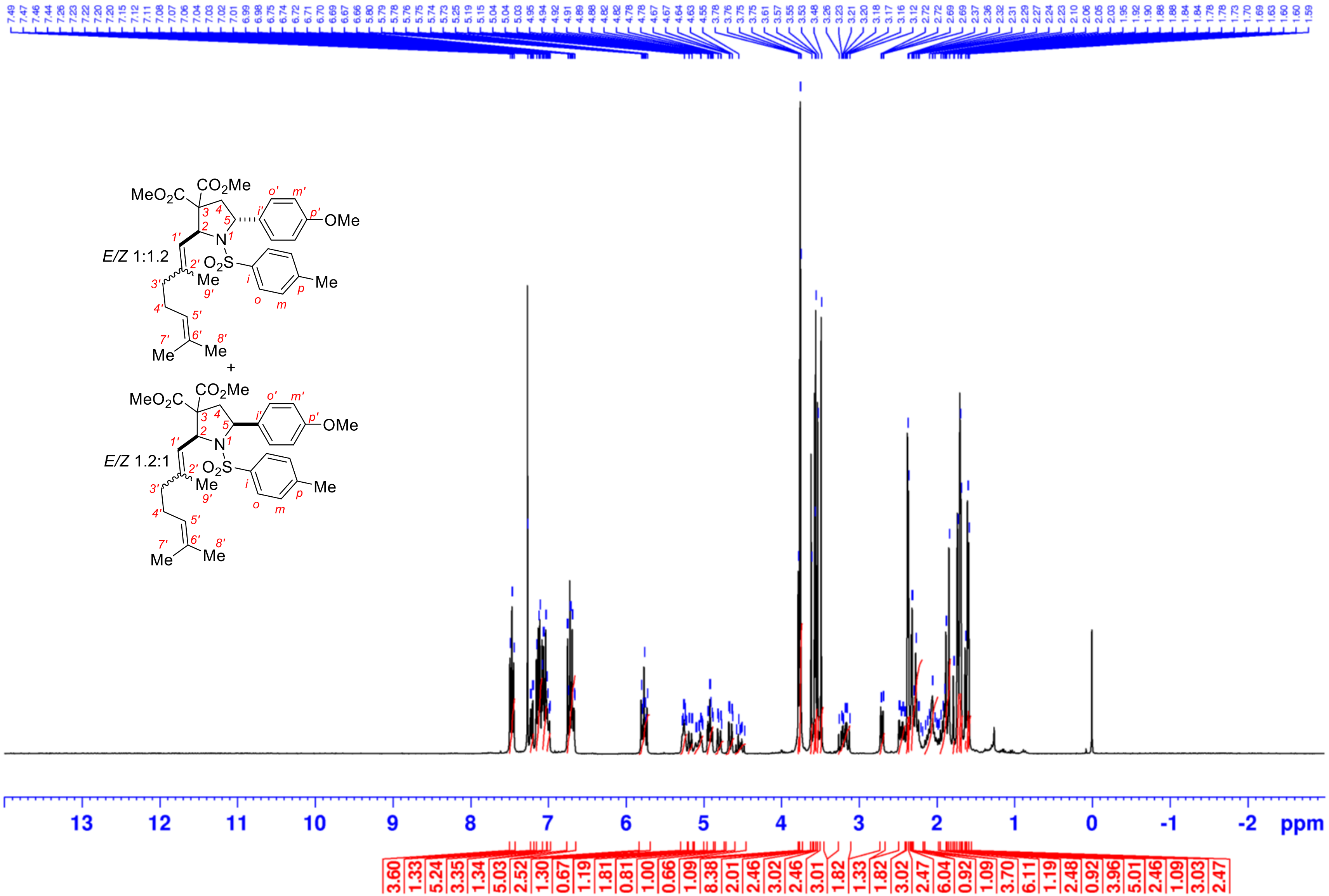


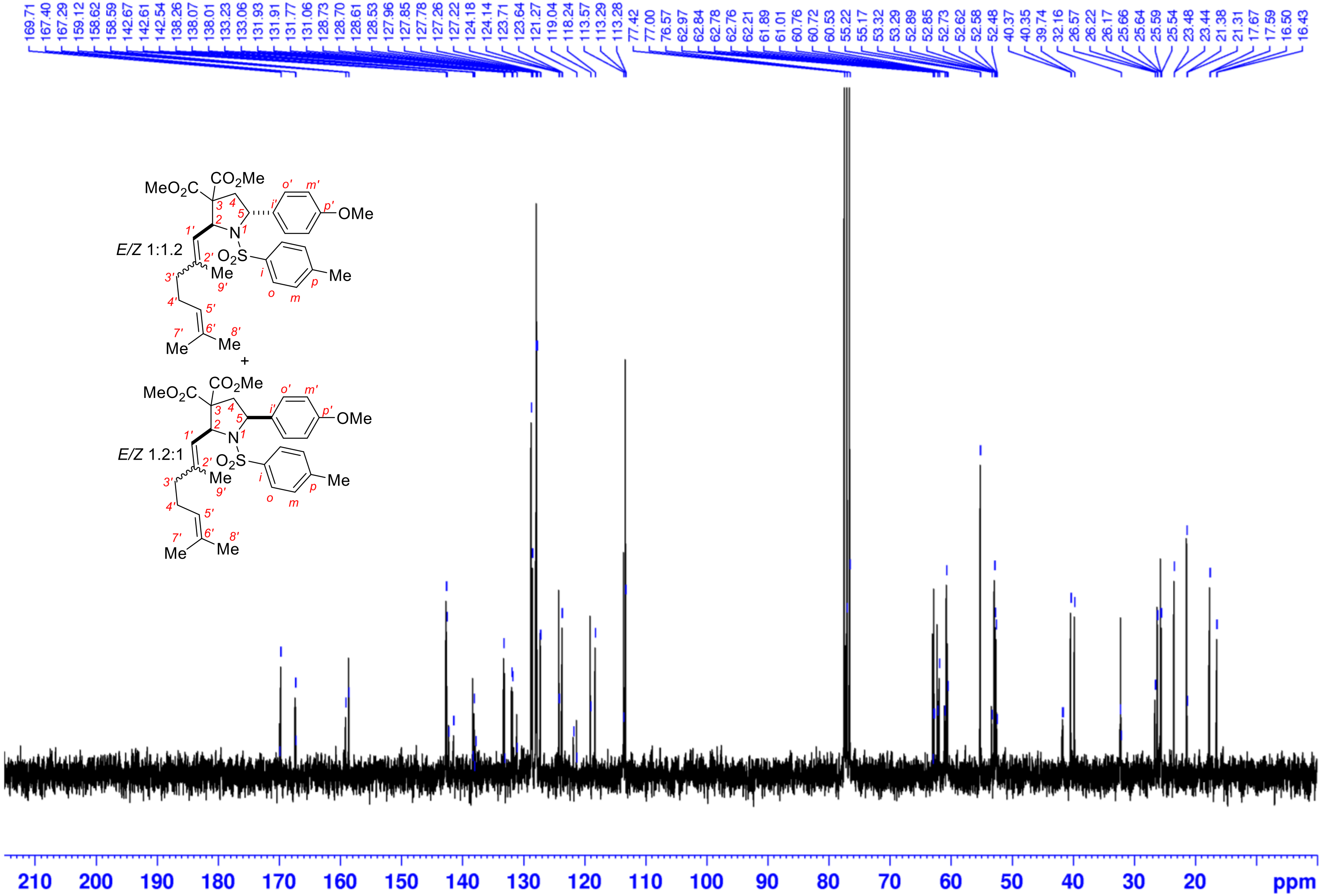

$^{1}H,^{13}C$-HMBC NMR spectrum of 2*Z*-**2c**, 1*E*/1*Z* 2:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)



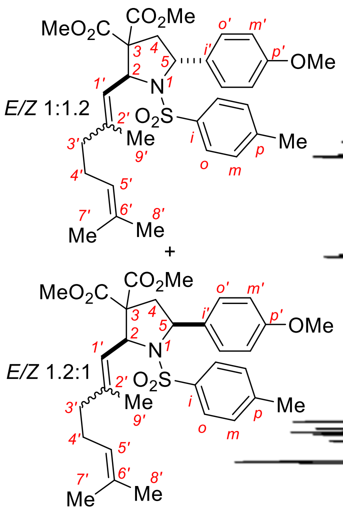

$^{1}$H NMR spectrum of 1*E*-**2c**, 2*E*/2*Z* 1.2:1 (300.1 MHz, $CDCl_3$)

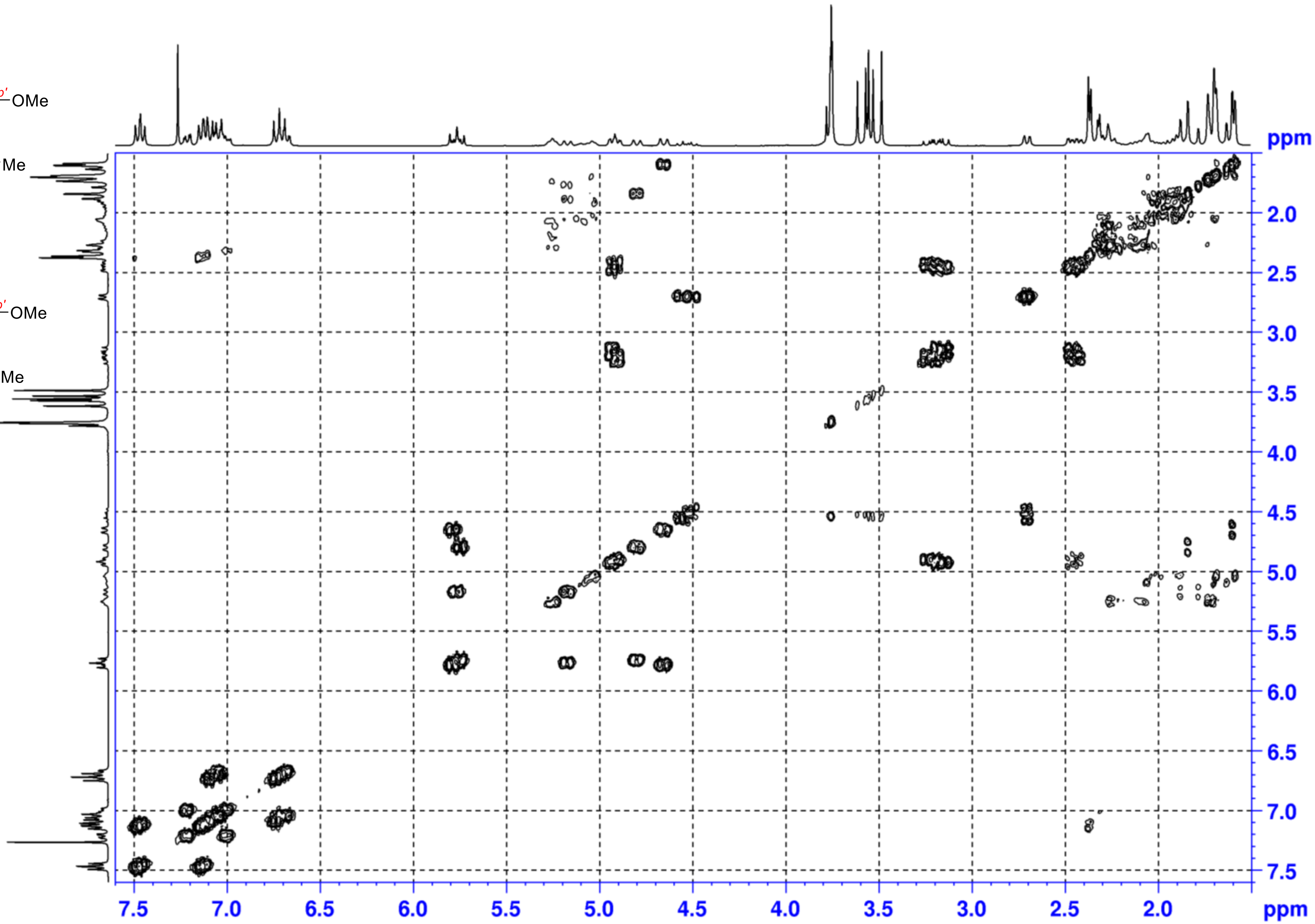



[1]H NMR spectrum of **6a**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 2.7:1 (300.1 MHz, $CDCl_3$)

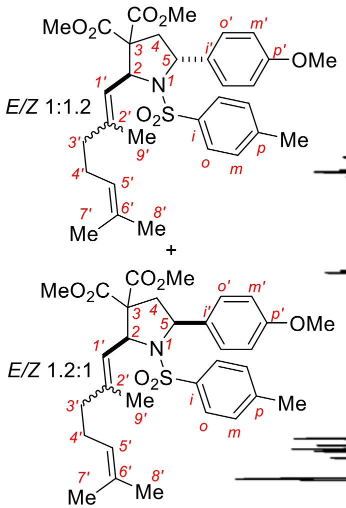


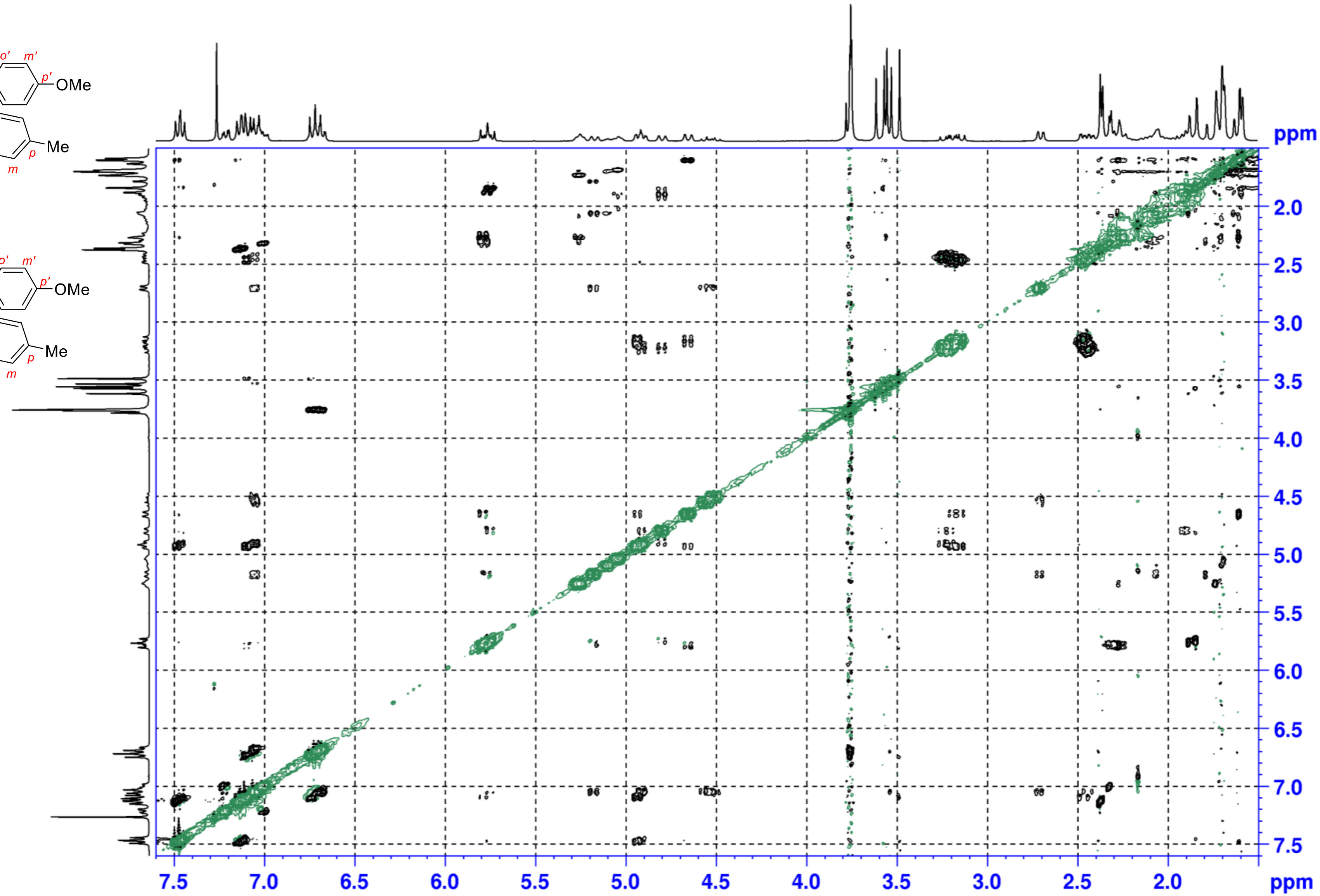

$^{13}$C NMR spectrum of **6a**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 2.7:1 (75.5 MHz, $CDCl_3$)



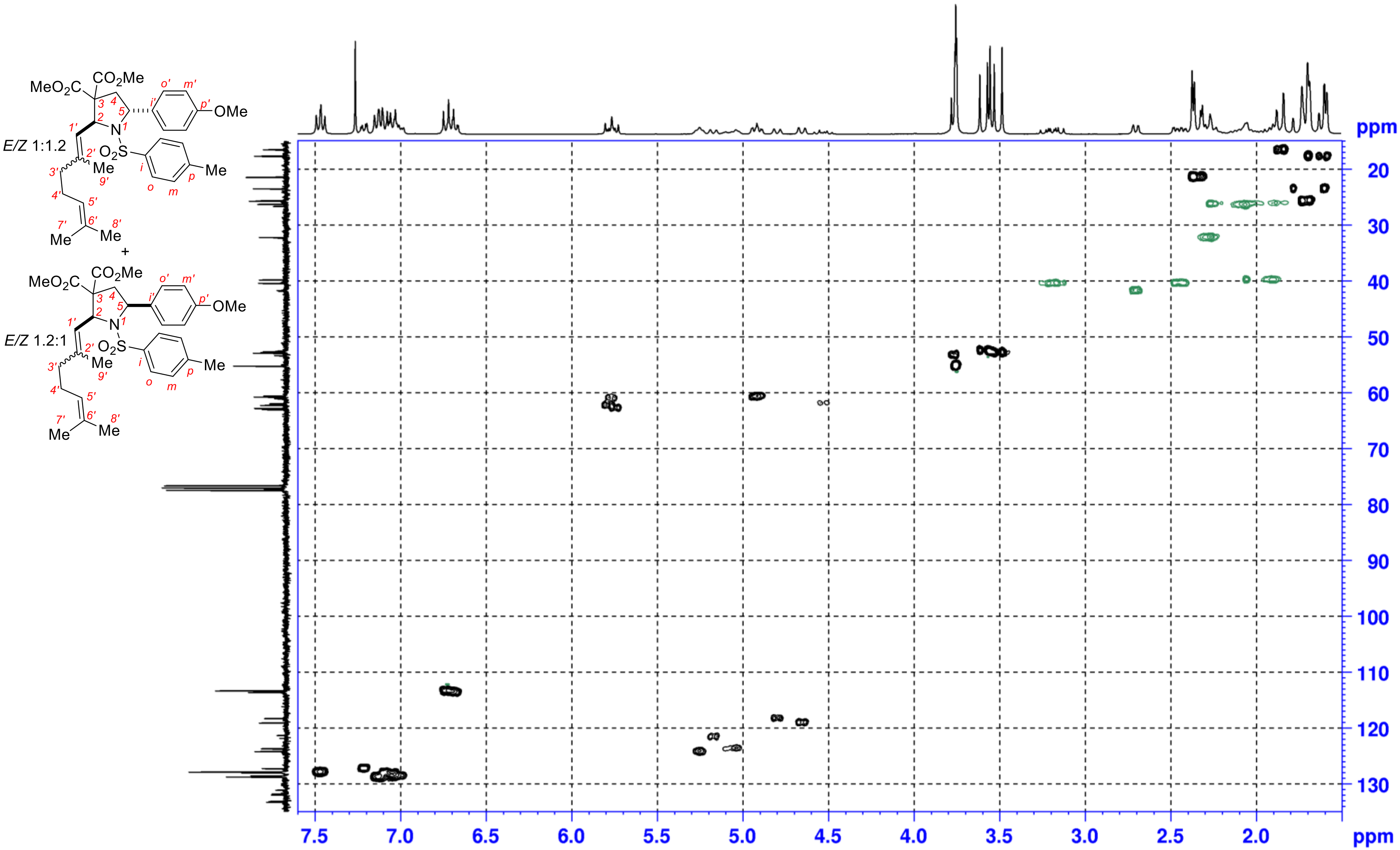




[1]H,[1]H-COSY NMR spectrum of **6a**, *trans* (*E*/*Z* 1:1.2)/*cis* (*E*/*Z* 1.2:1) 2.7:1 (300.1 MHz, $CDCl_3$)

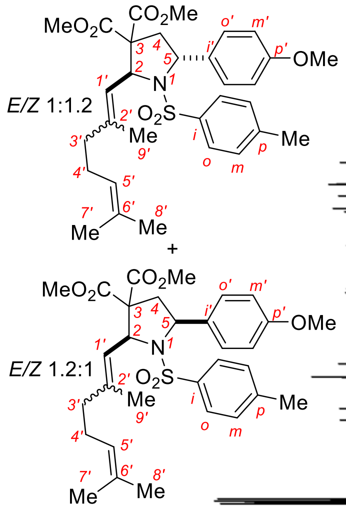


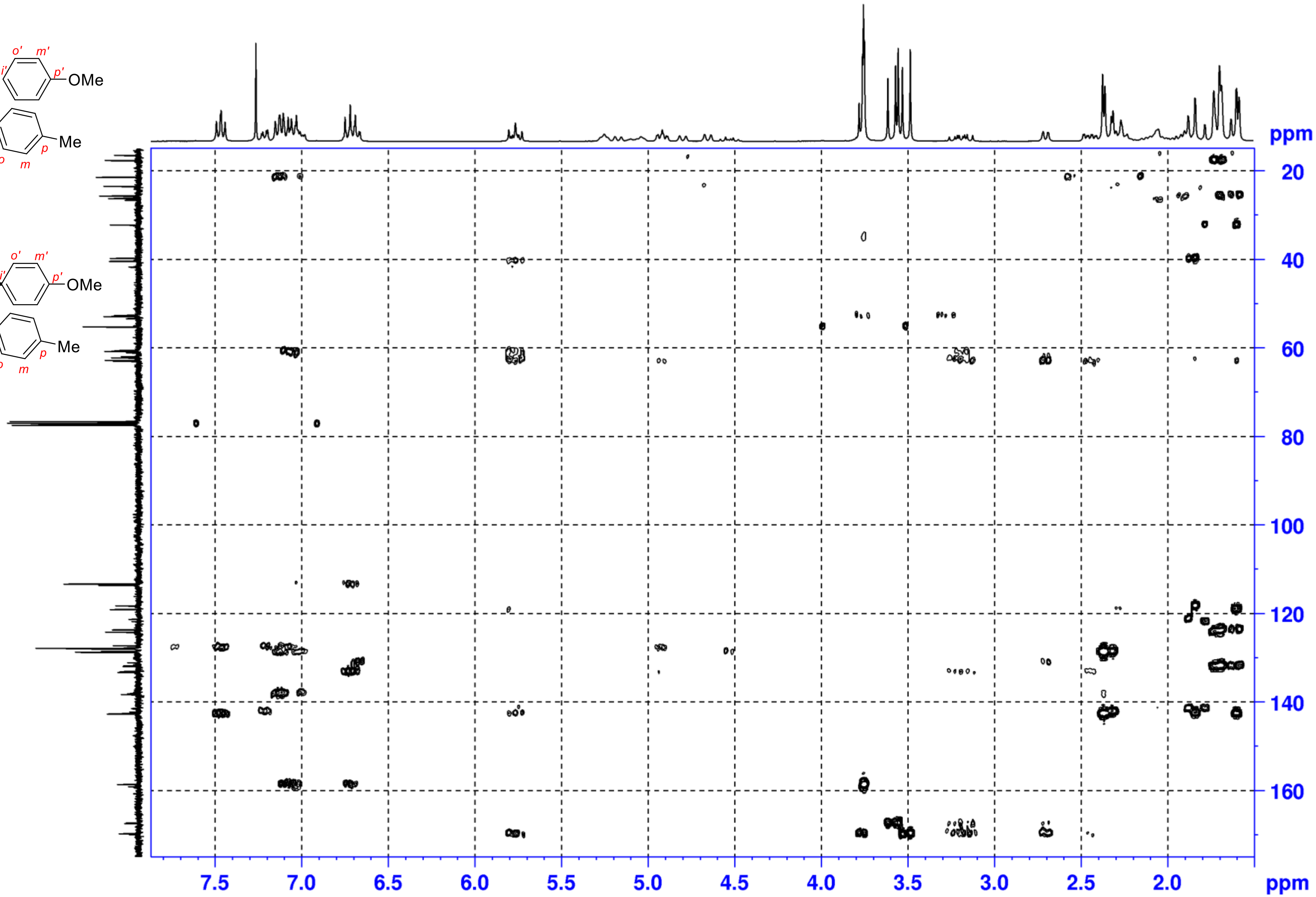




[1]H,[1]H-NOESY NMR spectrum of **6a**, *trans* (*E*/*Z* 1:1.2)/*cis* (*E*/*Z* 1.2:1) 2.7:1 (300.1 MHz, $CDCl_3$)

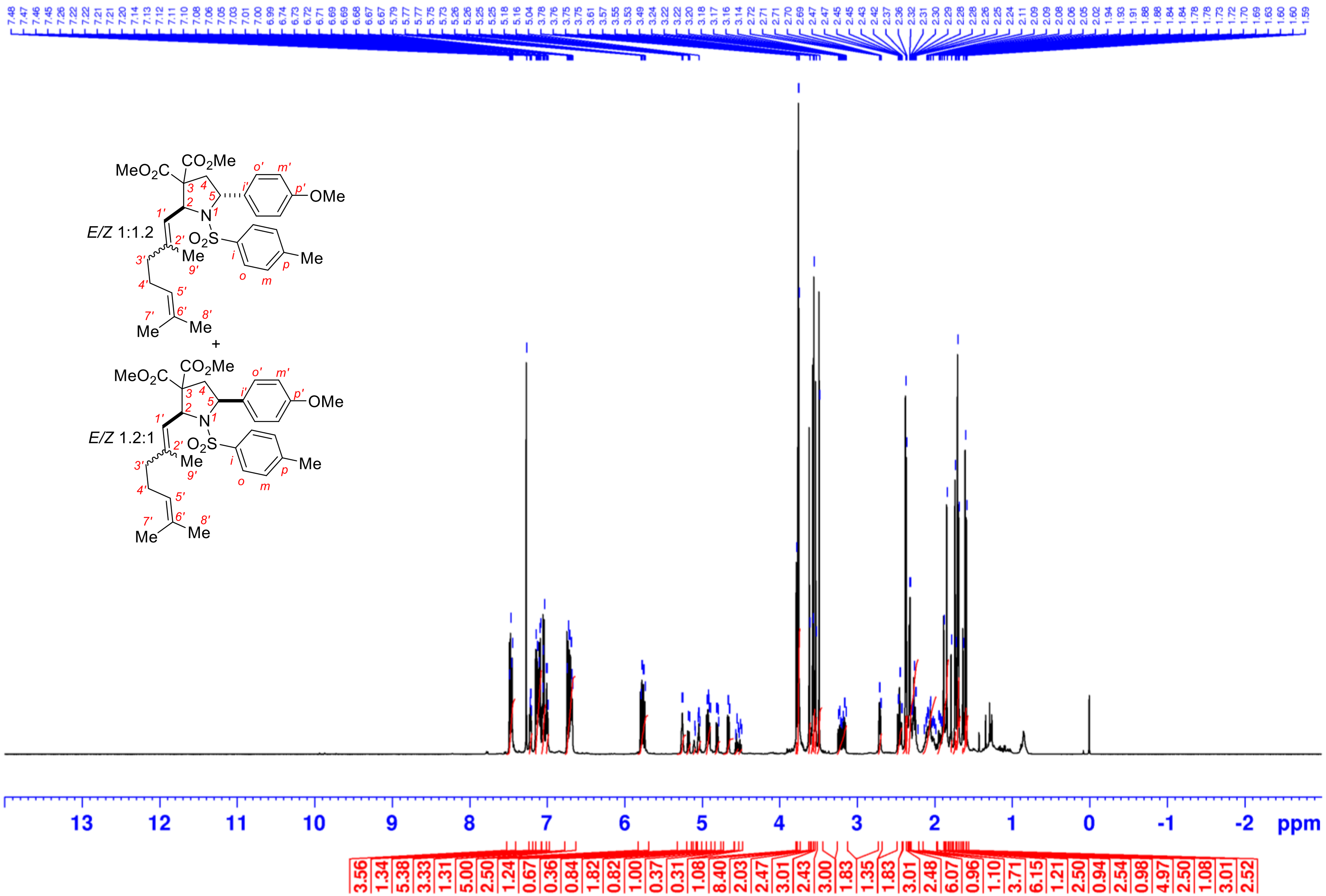


$^{1}$H,$^{13}$C-edited-HSQC NMR spectrum of **6a**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 2.7:1 ($^{1}$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)

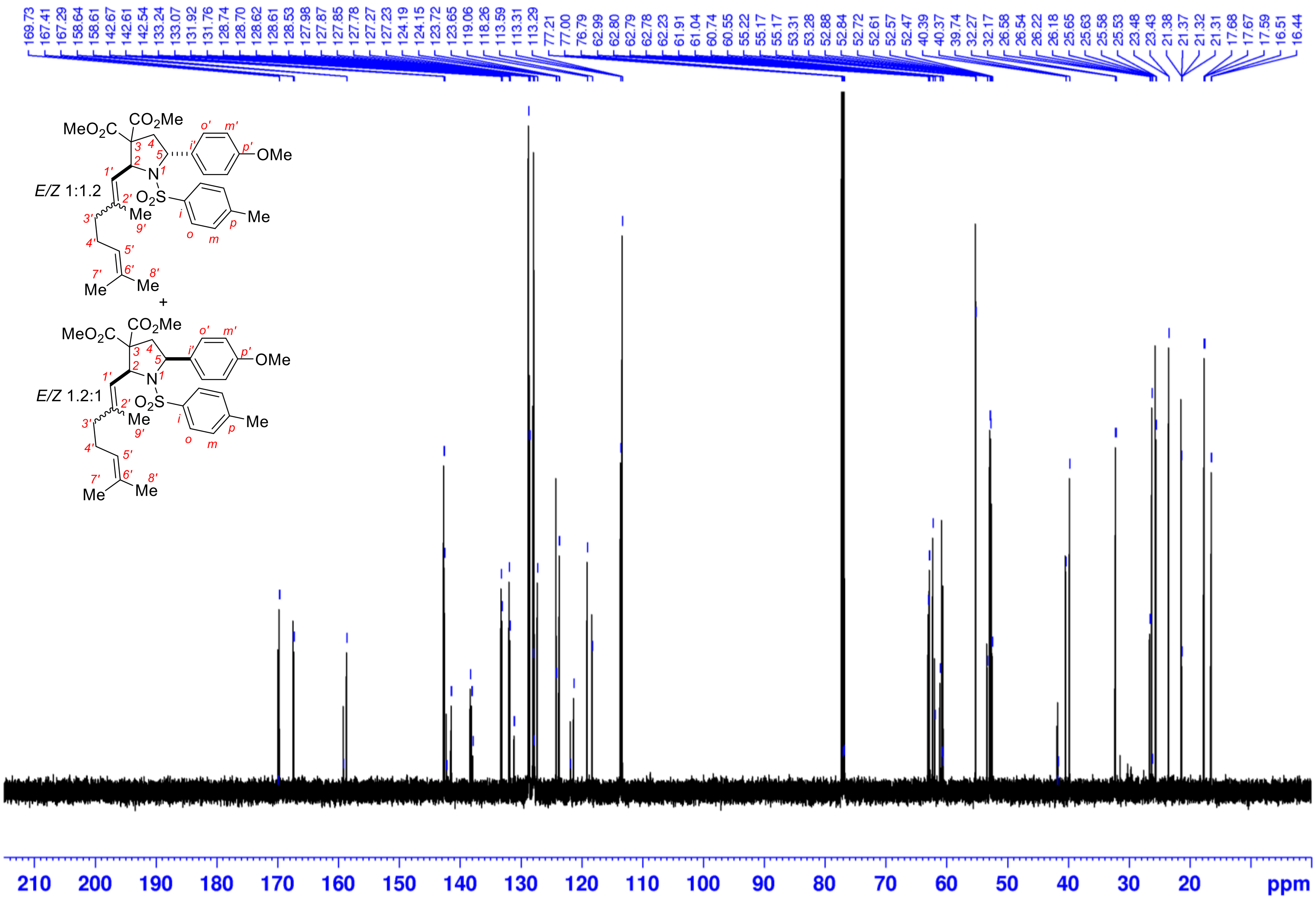




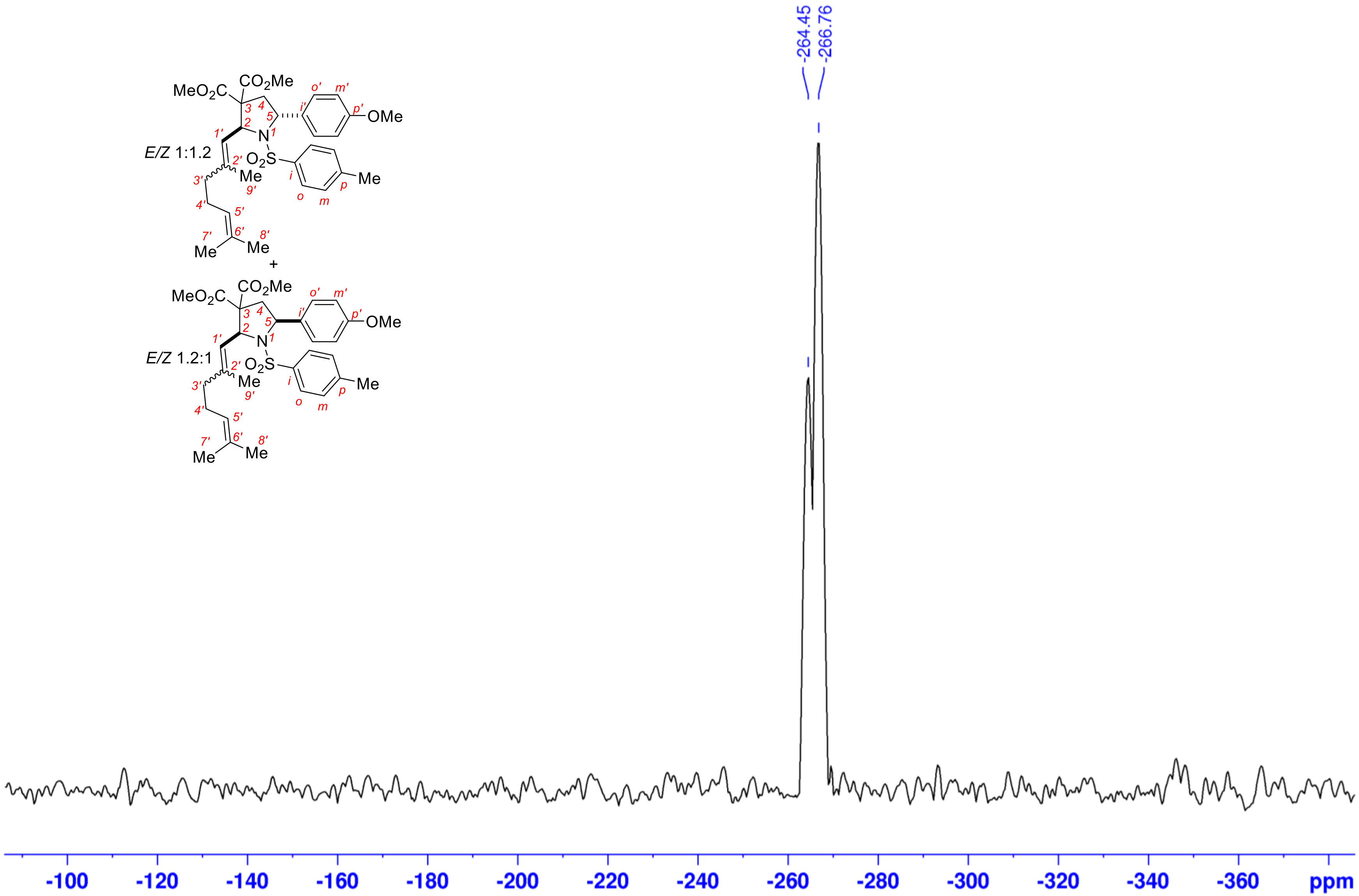
$^{1}H,^{13}C$-HMBC NMR spectrum of **6a**, *trans* (*E*/*Z* 1:1.2)/*cis* (*E*/*Z* 1.2:1) 2.7:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)



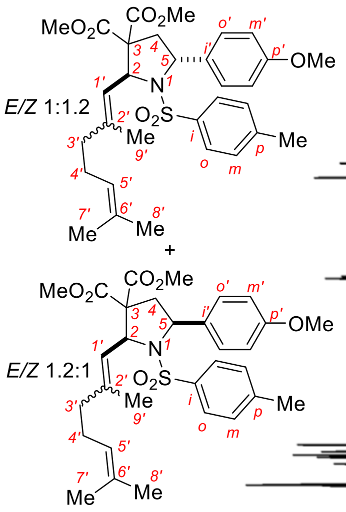
[1]H NMR spectrum of **6a**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 2.7:1 (600.1 MHz, $CDCl_3$)

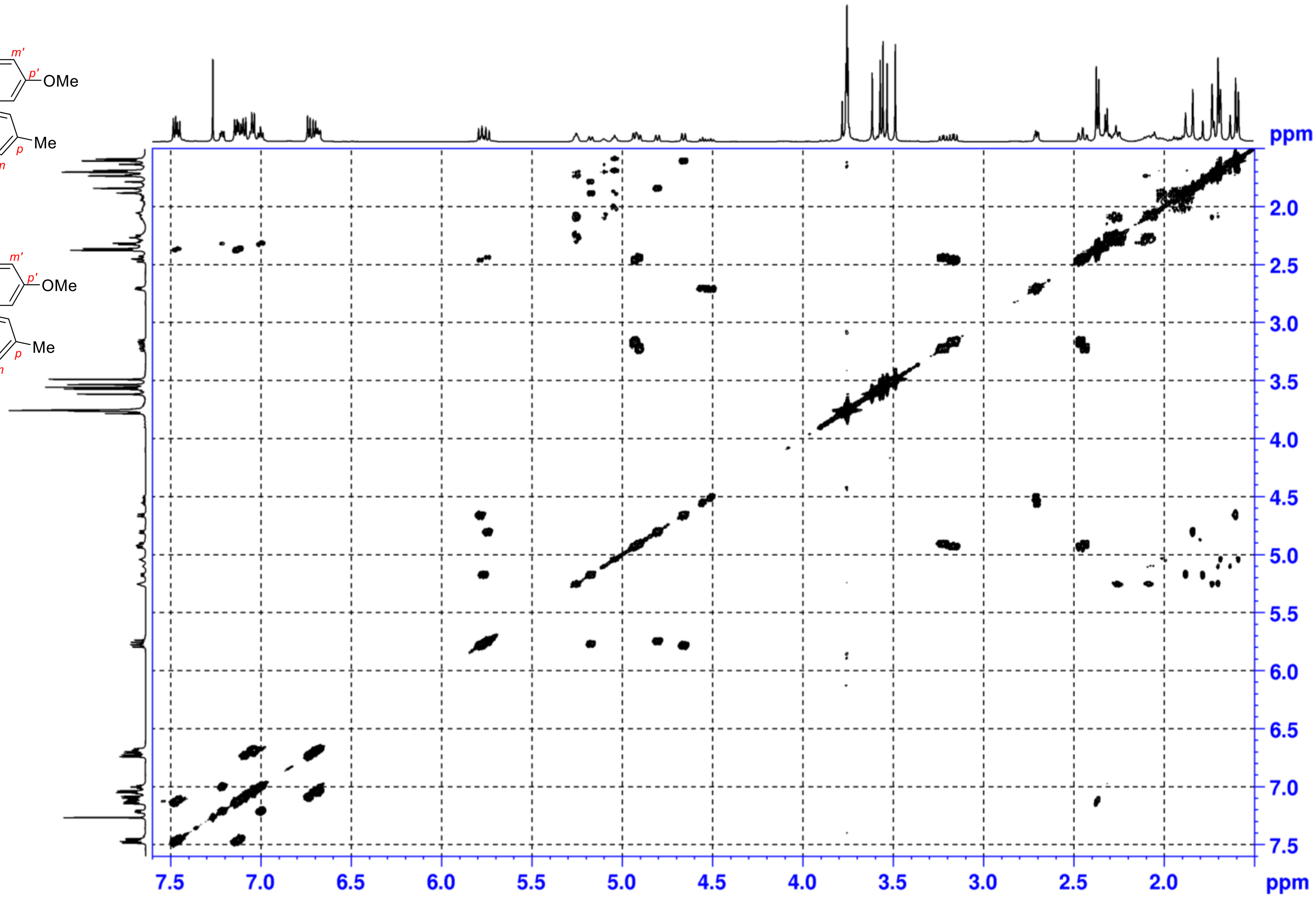


$^{13}$C NMR spectrum of **6a**, *trans* (*E*/*Z* 1:1.2)/*cis* (*E*/*Z* 1.2:1) 2.7:1 (150.9 MHz, $CDCl_3$)

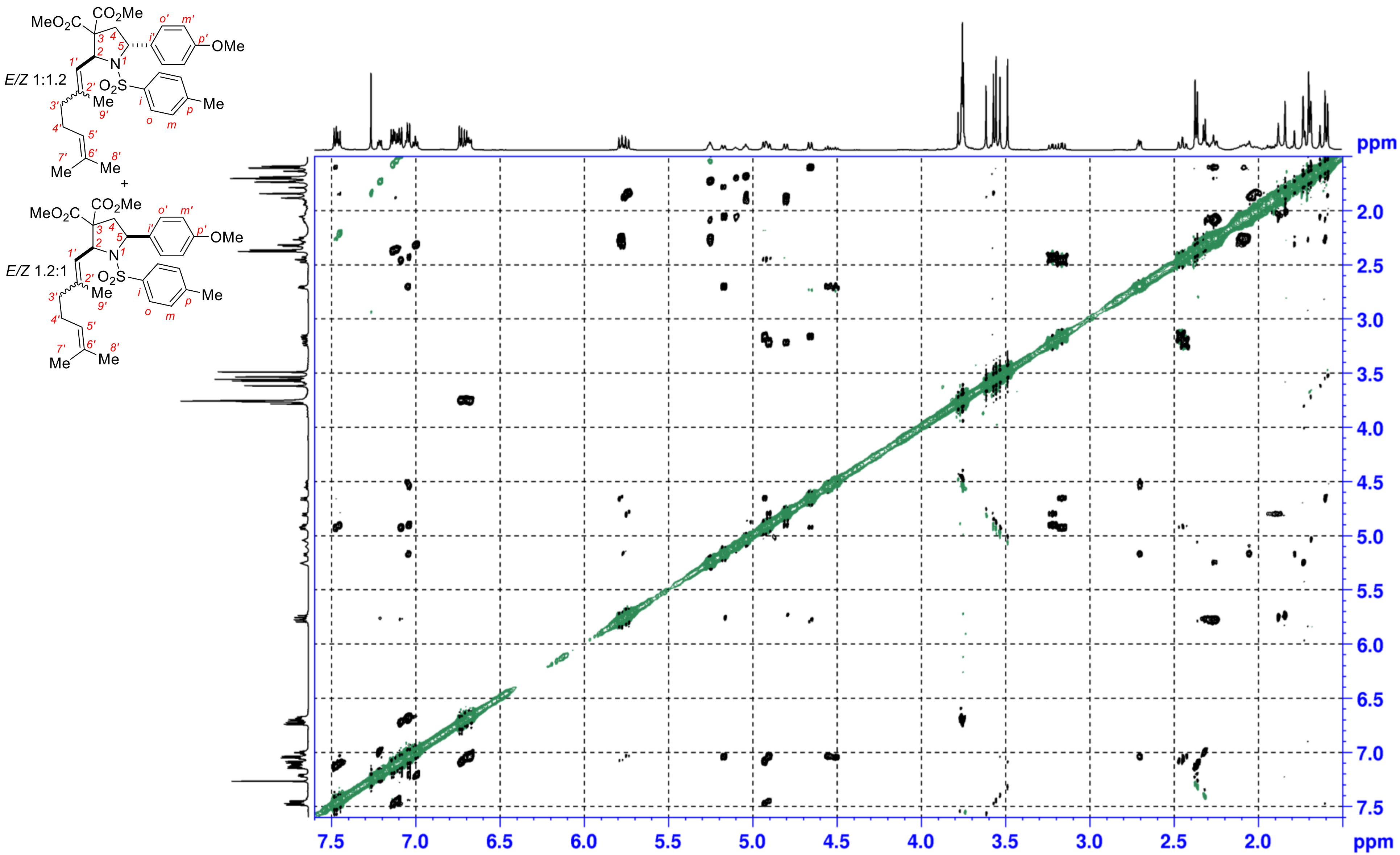



$^{15}$N NMR spectrum of **6a**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 2.7:1 (60.8 MHz, $CDCl_3$; reconstructed from $^1H$–$^{15}N$ HMBC)

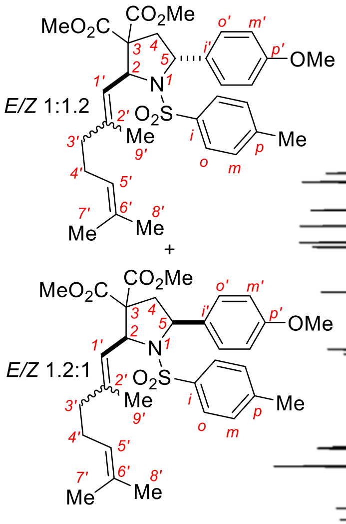


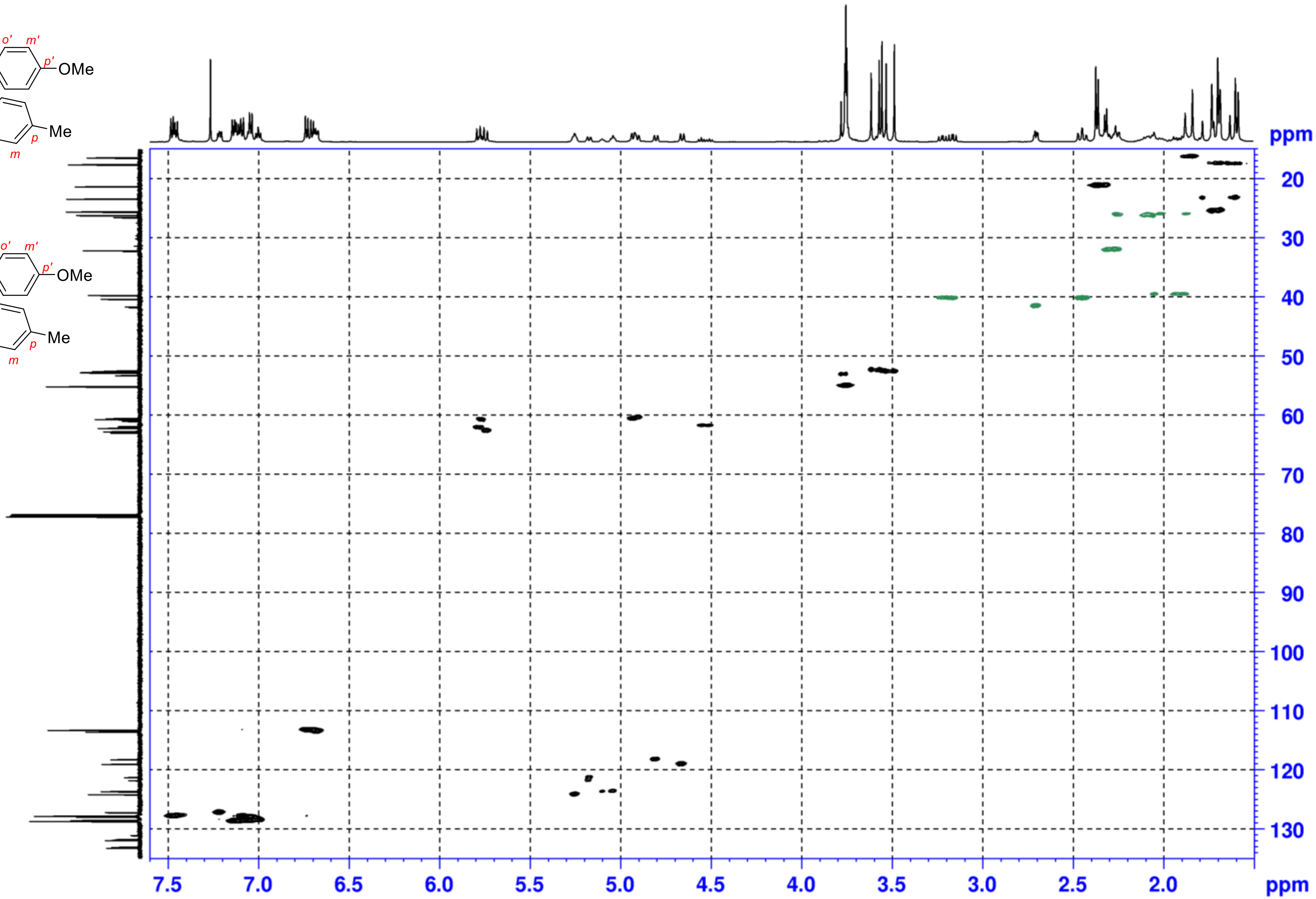



[1]H,[1]H-COSY NMR spectrum of **6a**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 2.7:1 (600.1 MHz, $CDCl_3$)

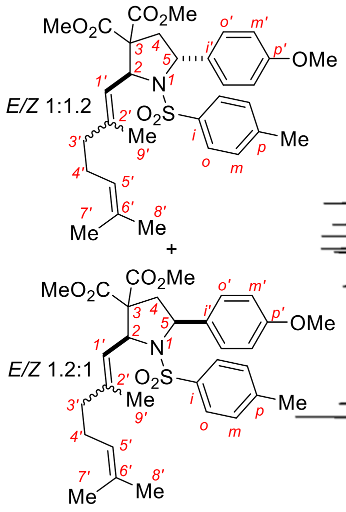


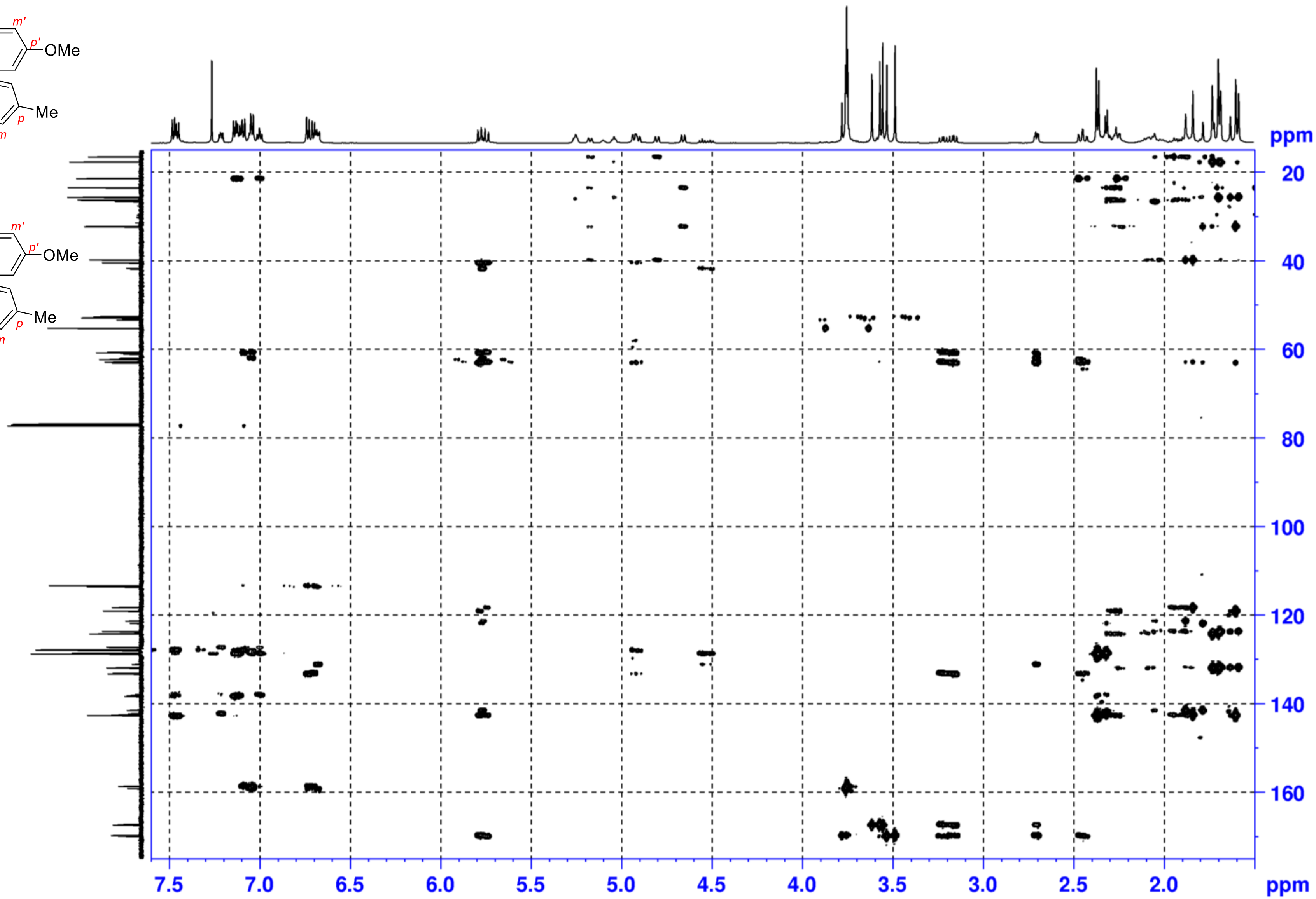

$^{1}H,^{1}H$-NOESY NMR spectrum of **6a**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 2.7:1 (600.1 MHz, $CDCl_3$)



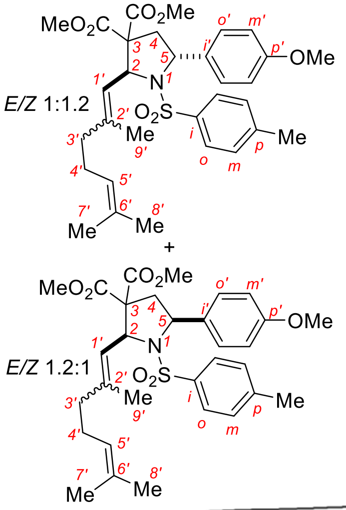



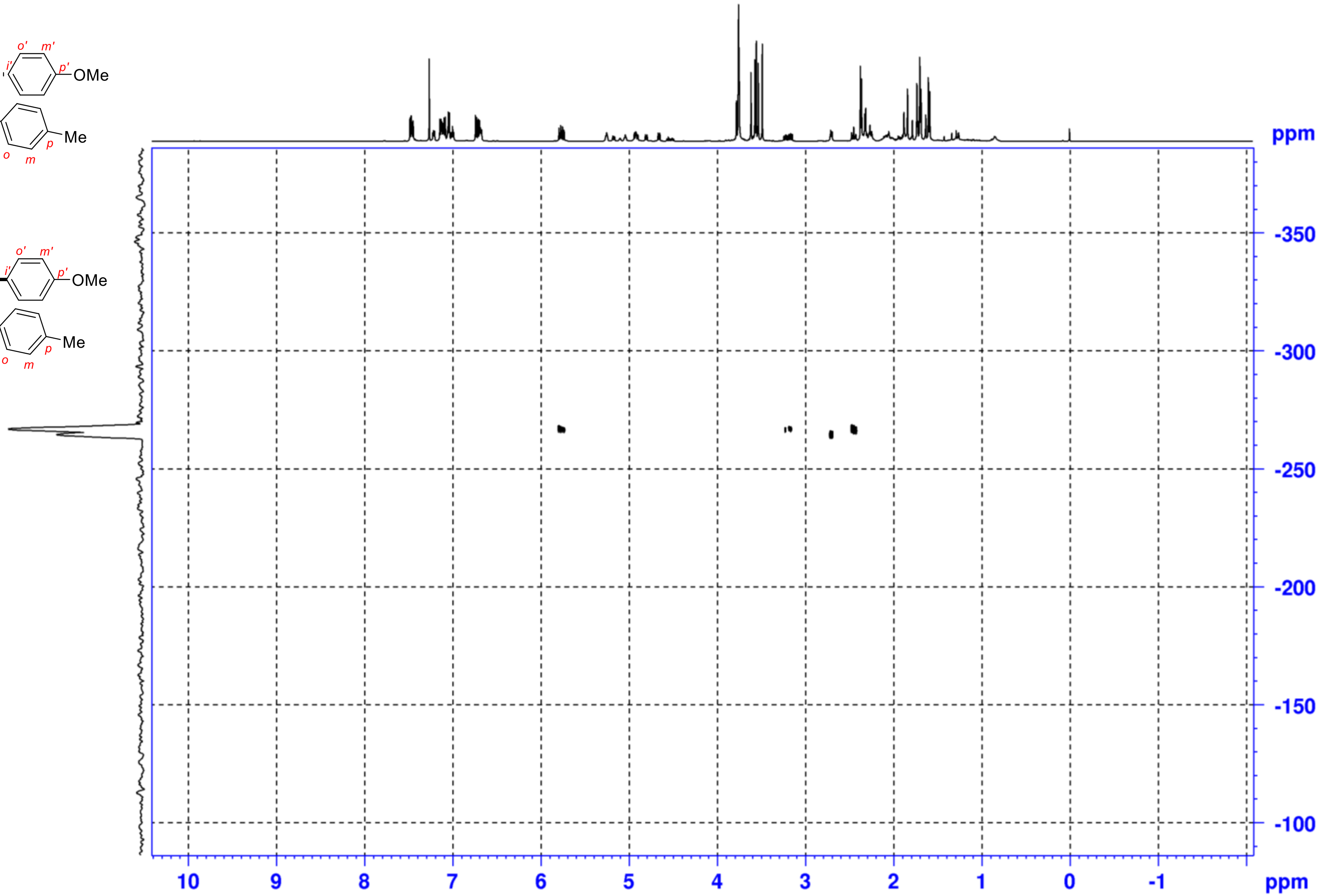
$^{1}H,^{13}C$-edited-HSQC NMR spectrum of **6a**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 2.7:1 ($^{1}H$: 600.1 MHz; $^{13}C$: 150.9 MHz; $CDCl_3$)



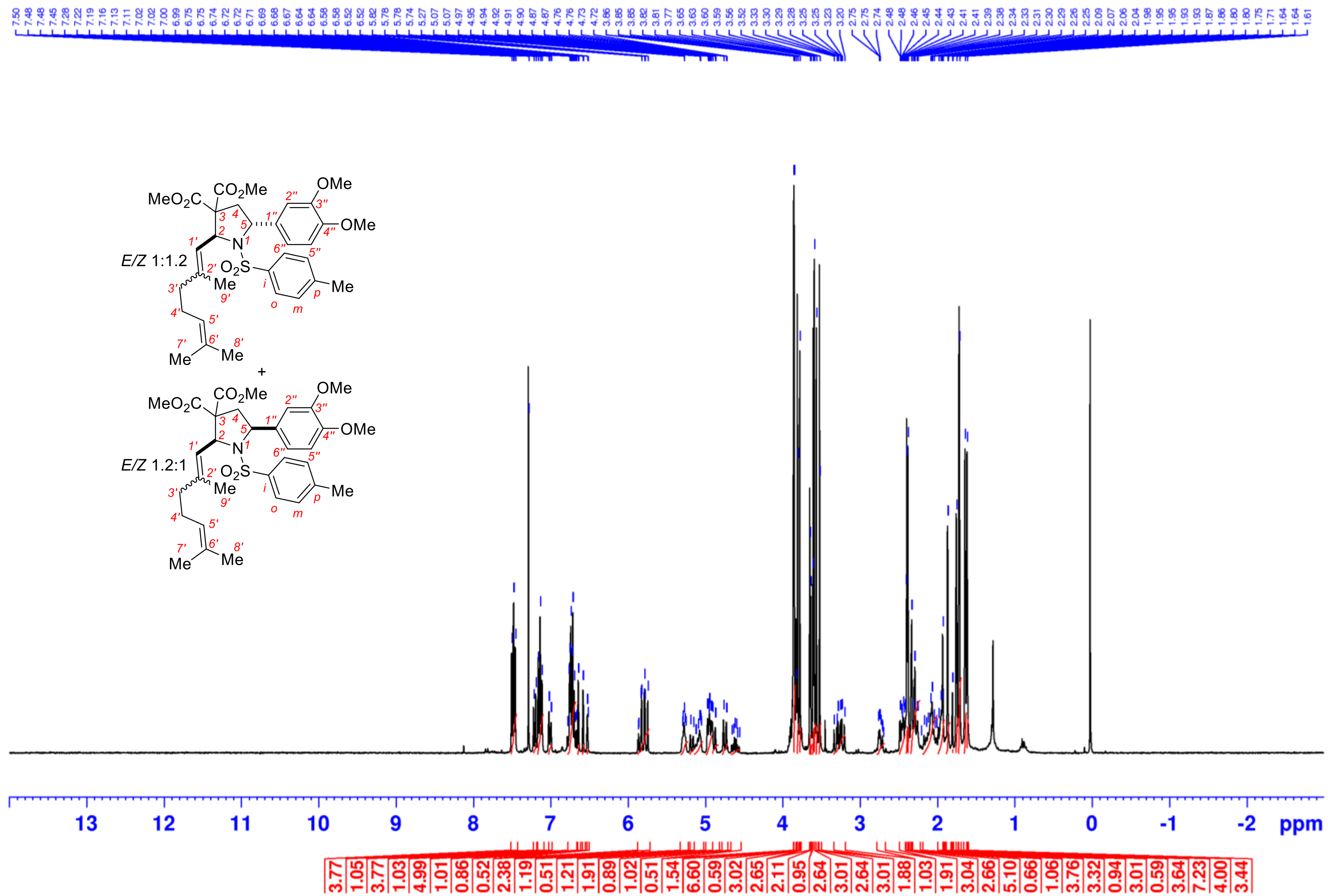




$^{1}H$,$^{13}C$-HMBC NMR spectrum of **6a**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 2.7:1 ($^{1}H$: 600.1 MHz; $^{13}C$: 150.9 MHz; $CDCl_3$)

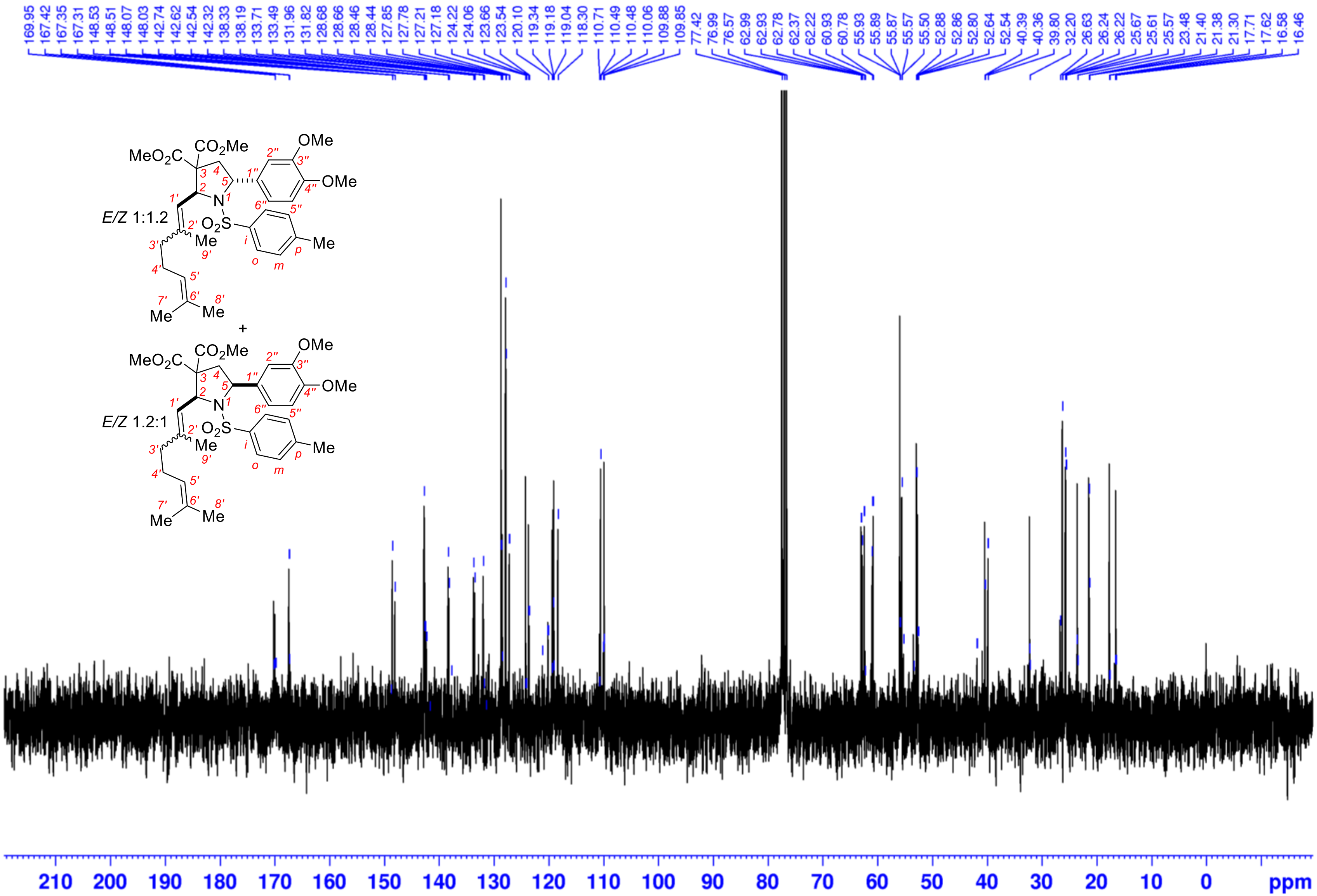


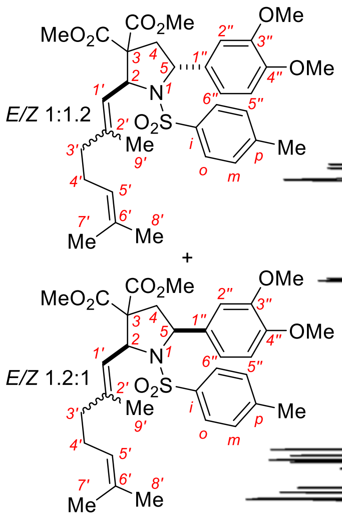

$^{1}H,^{15}N$-HMBC NMR spectrum of **6a**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 2.7:1 ($^{1}H$: 600.1 MHz; $^{15}N$: 60.8 MHz; $CDCl_3$)

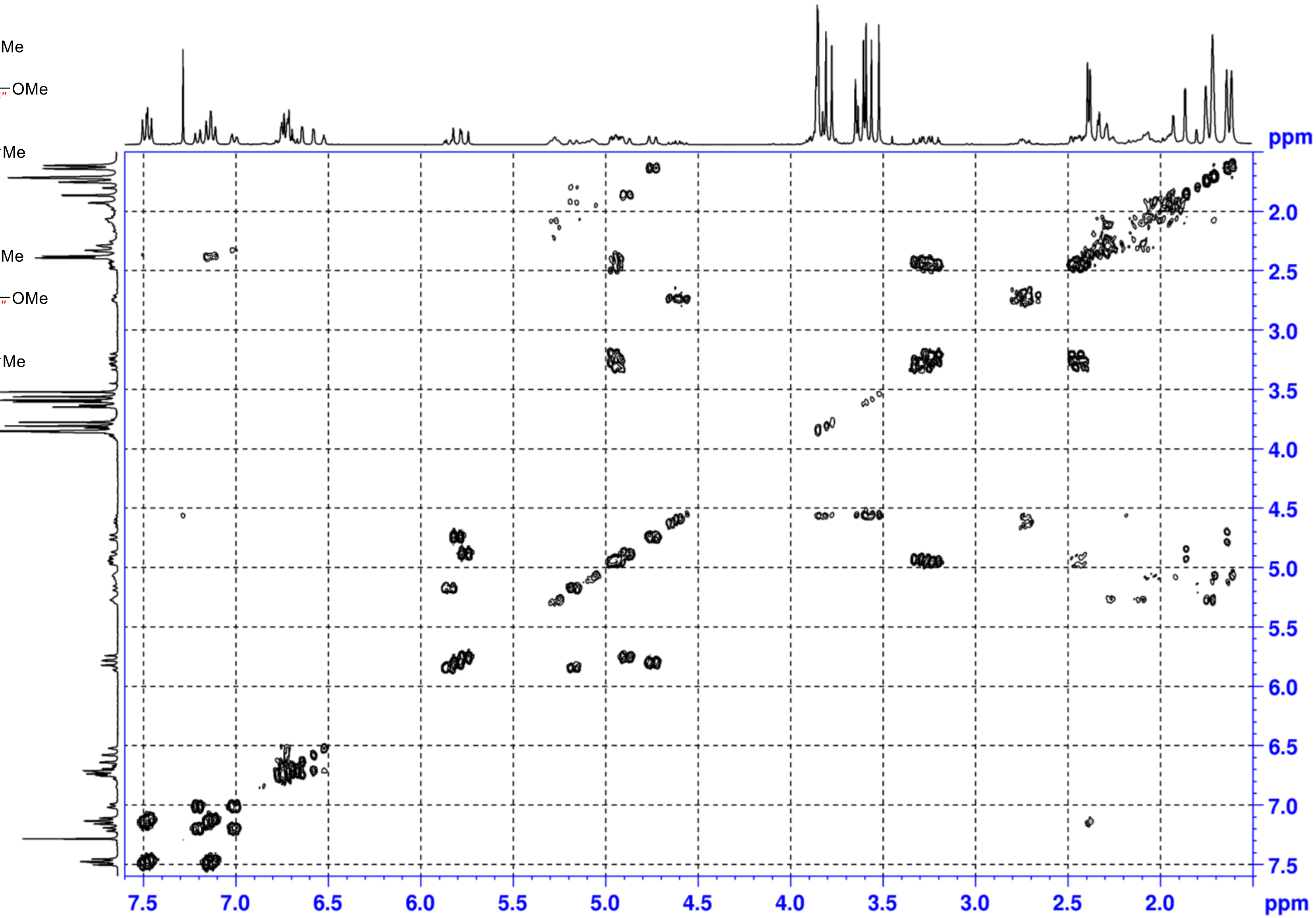


[1]H NMR spectrum of **6b**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 3.7:1 (300.1 MHz, $CDCl_3$)

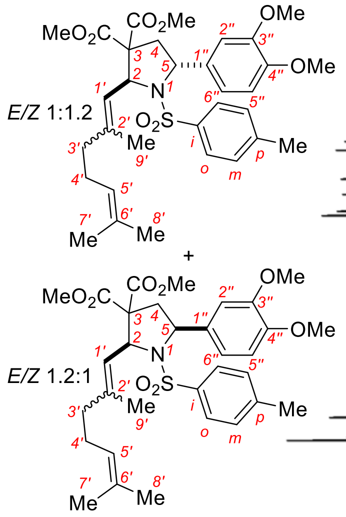


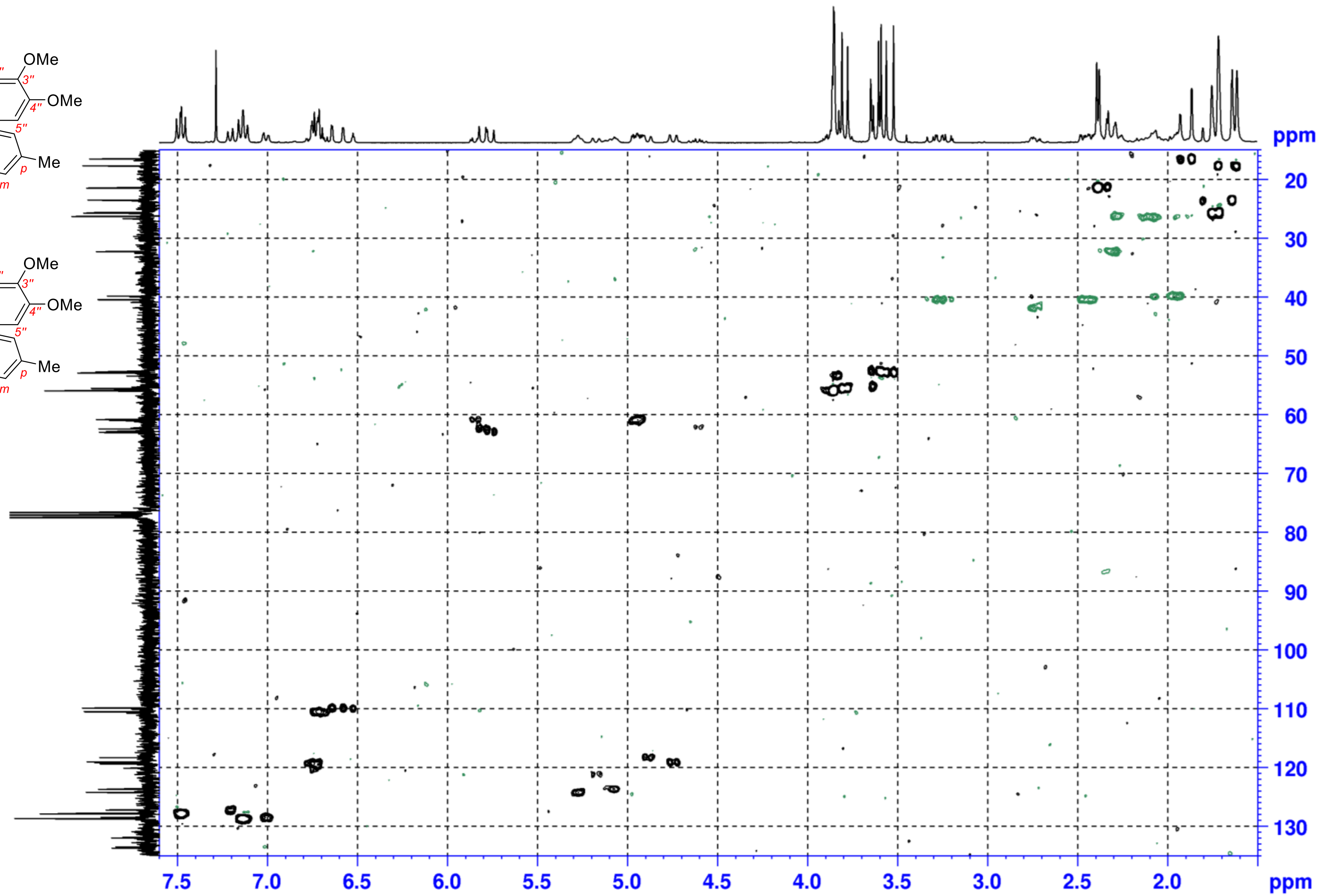
$^{13}$C NMR spectrum of **6b**, *trans* (*E*/*Z* 1:1.2)/*cis* (*E*/*Z* 1.2:1) 3.7:1 (75.5 MHz, $CDCl_3$)



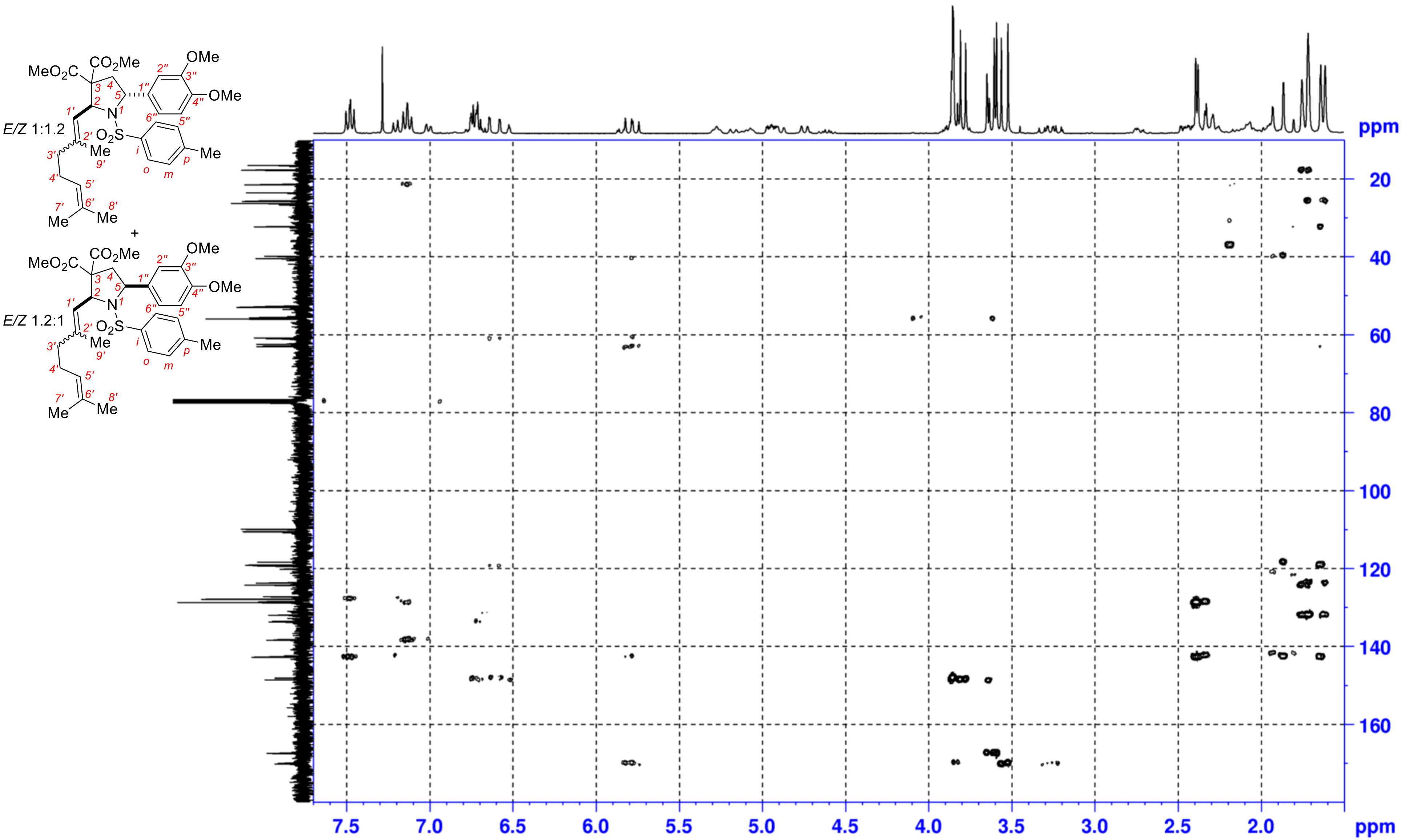


$^{1}H,^{1}H$-COSY NMR spectrum of **6b**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 3.7:1 (300.1 MHz, $CDCl_3$)

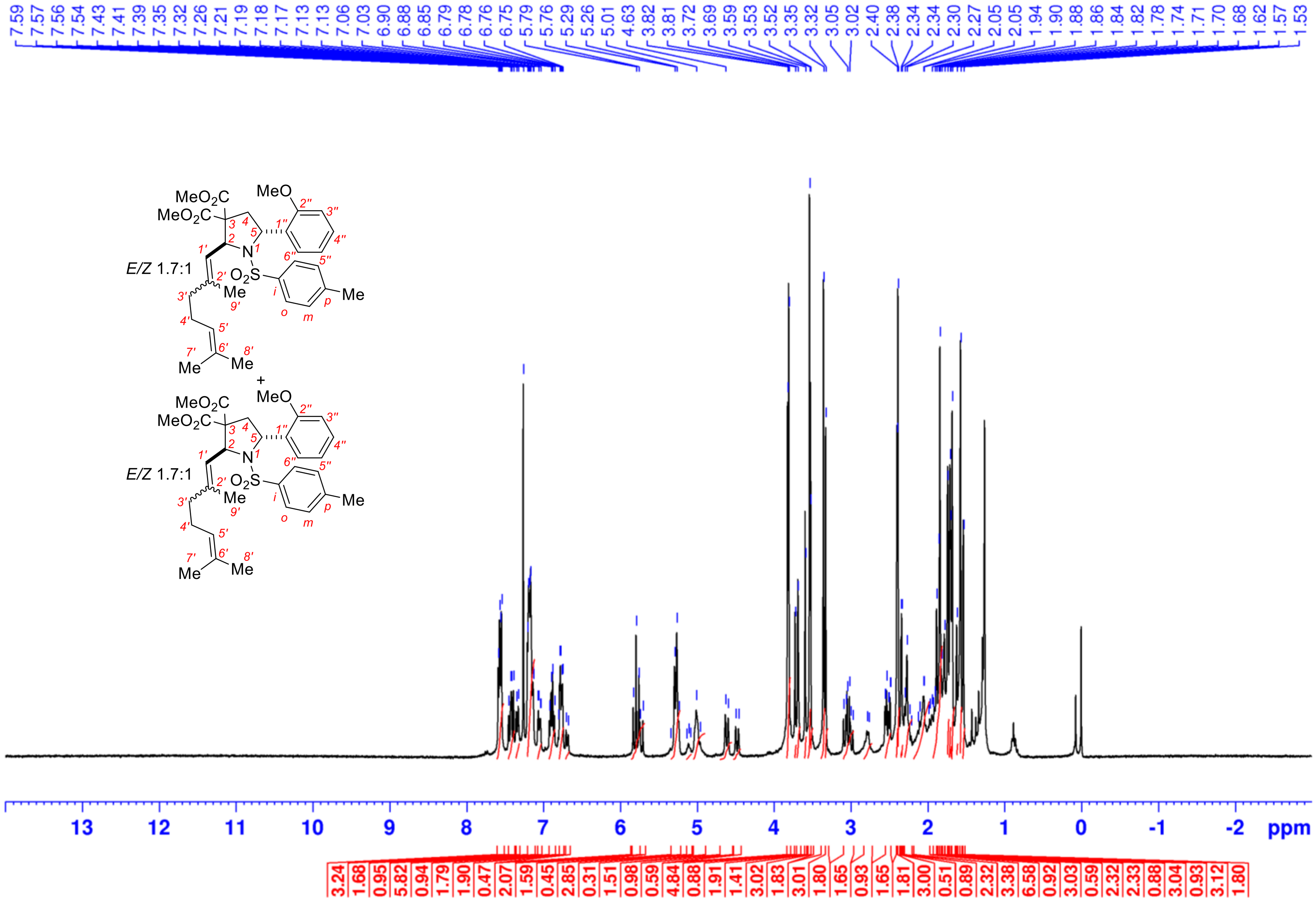




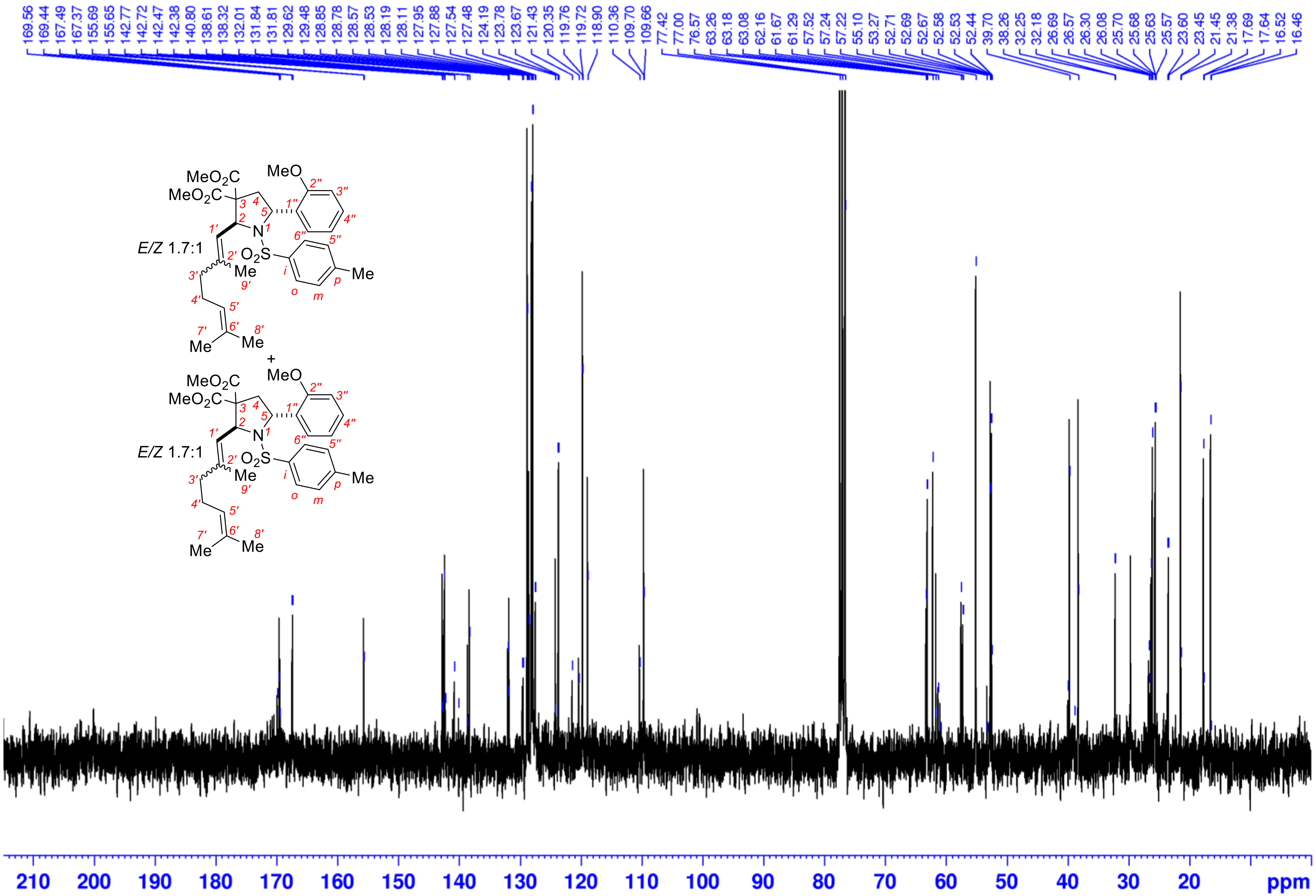
$^1$H,$^{13}$C-edited-HSQC NMR spectrum of **6b**, *trans* (*E/Z* 1:1.2)/*cis* (*E/Z* 1.2:1) 3.7:1 ($^1$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)



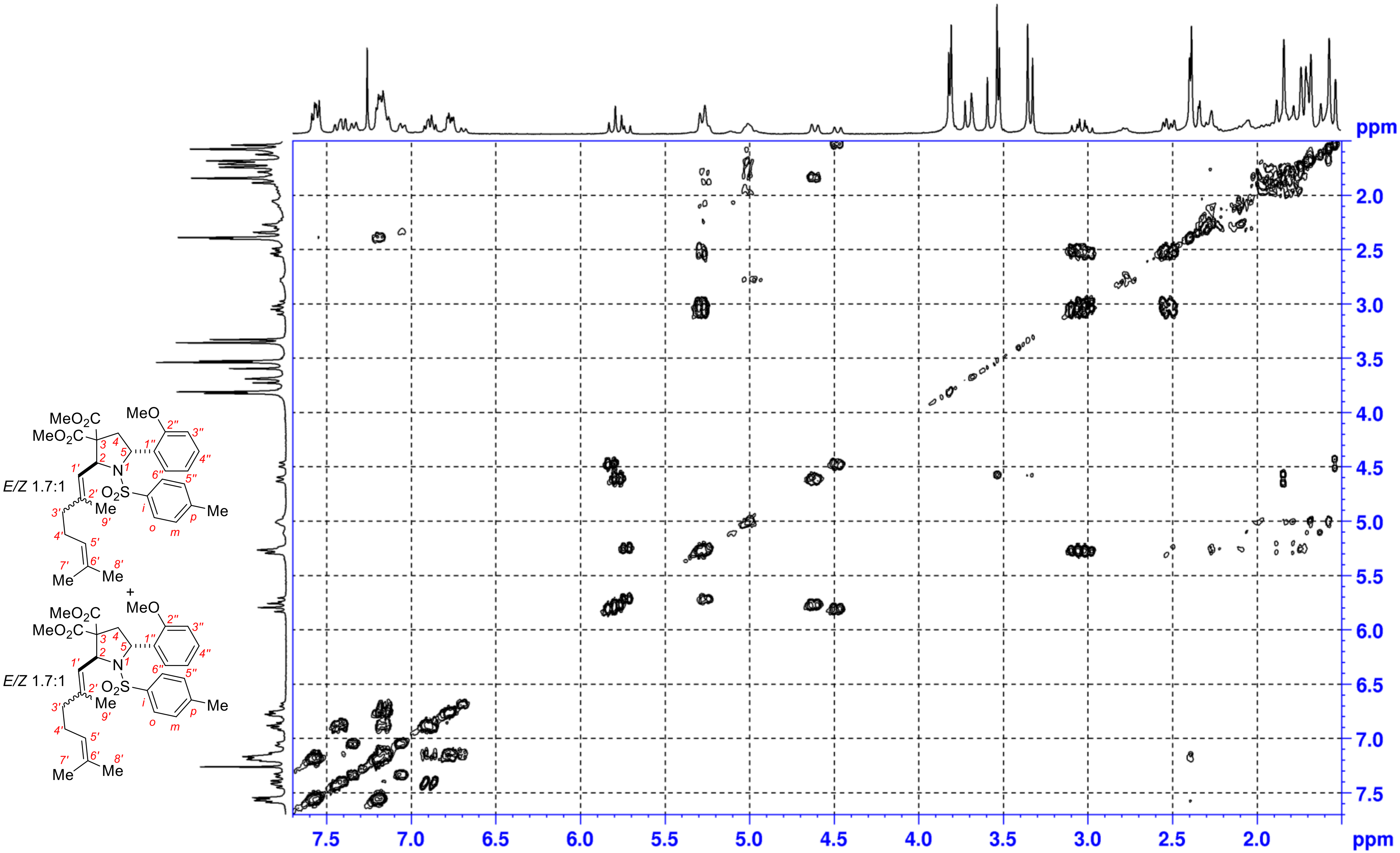

[1]H,[13]C-HMBC NMR spectrum of **6b**, *trans* (*E*/*Z* 1:1.2)/*cis* (*E*/*Z* 1.2:1) 3.7:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)



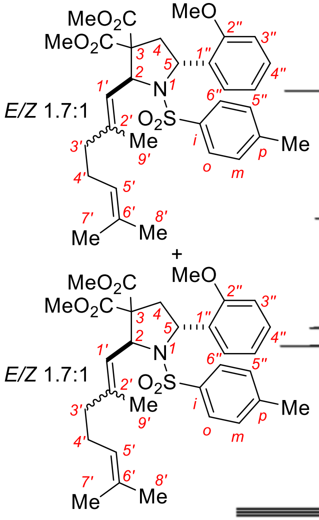
[1]H NMR spectrum of **6c**, *trans* (*E/Z* 1.7:1)/*cis* (*E/Z* 1.7:1) 3.5:1 (300.1 MHz, $CDCl_3$)

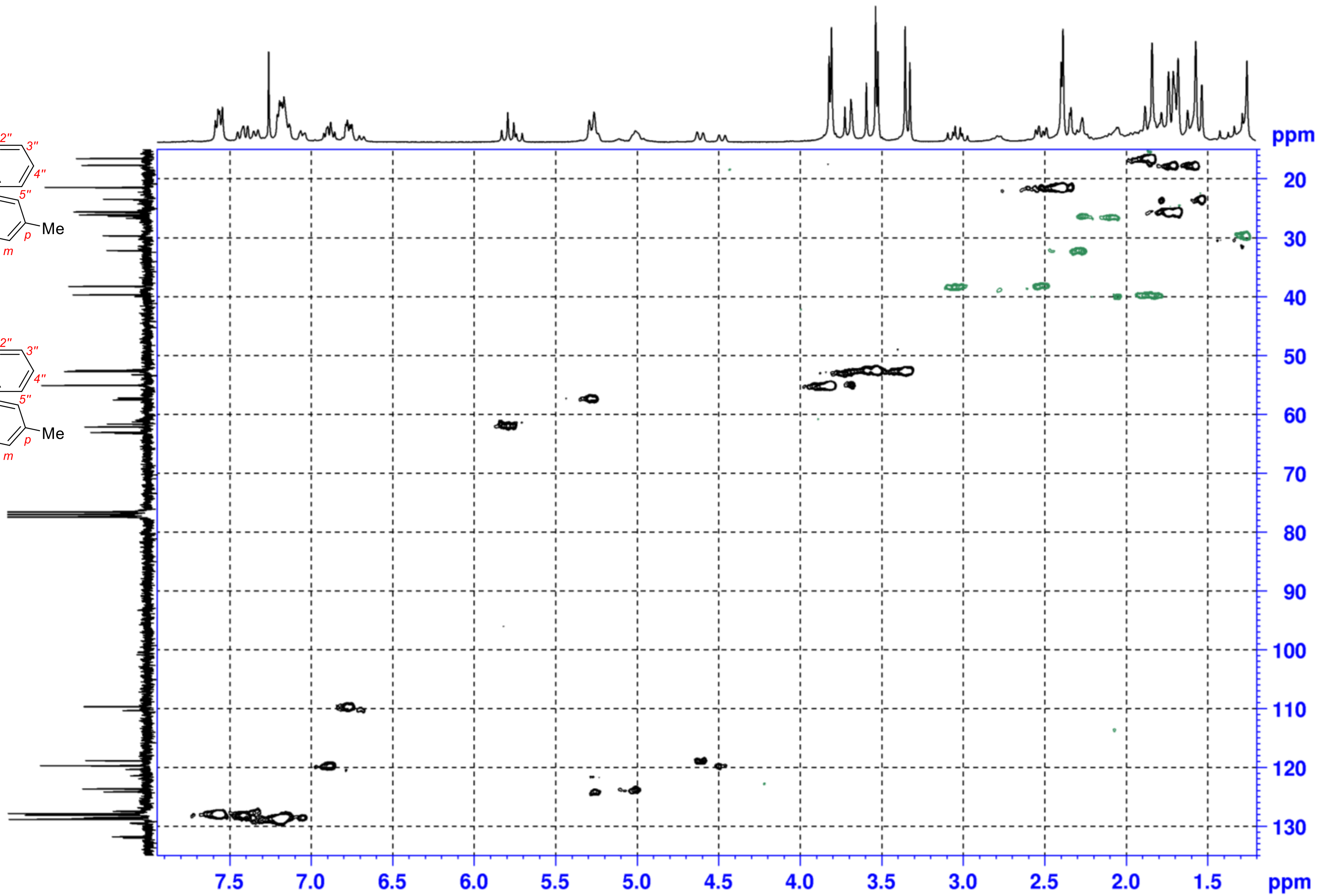



$^{13}C$ NMR spectrum of **6c**, *trans* (*E/Z* 1.7:1)/*cis* (*E/Z* 1.7:1) 3.5:1 (75.5 MHz, $CDCl_3$)

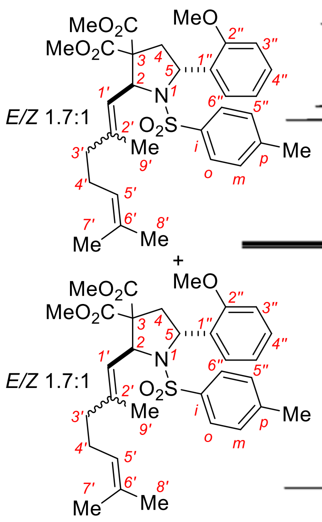


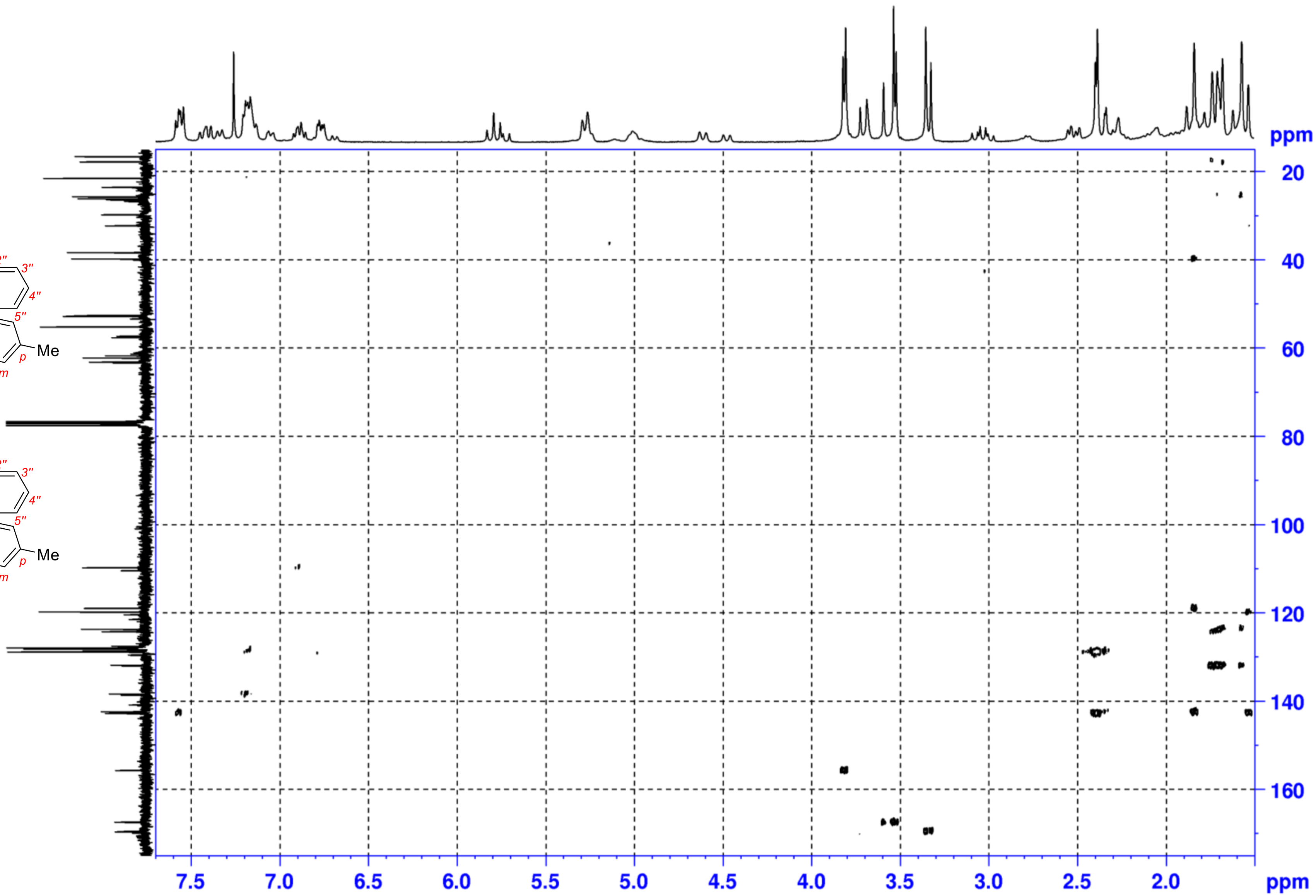

$^{1}H,^{1}H$-COSY NMR spectrum of **6c**, *trans* (*E*/*Z* 1.7:1)/*cis* (*E*/*Z* 1.7:1) 3.5:1 (300.1 MHz, $CDCl_3$)



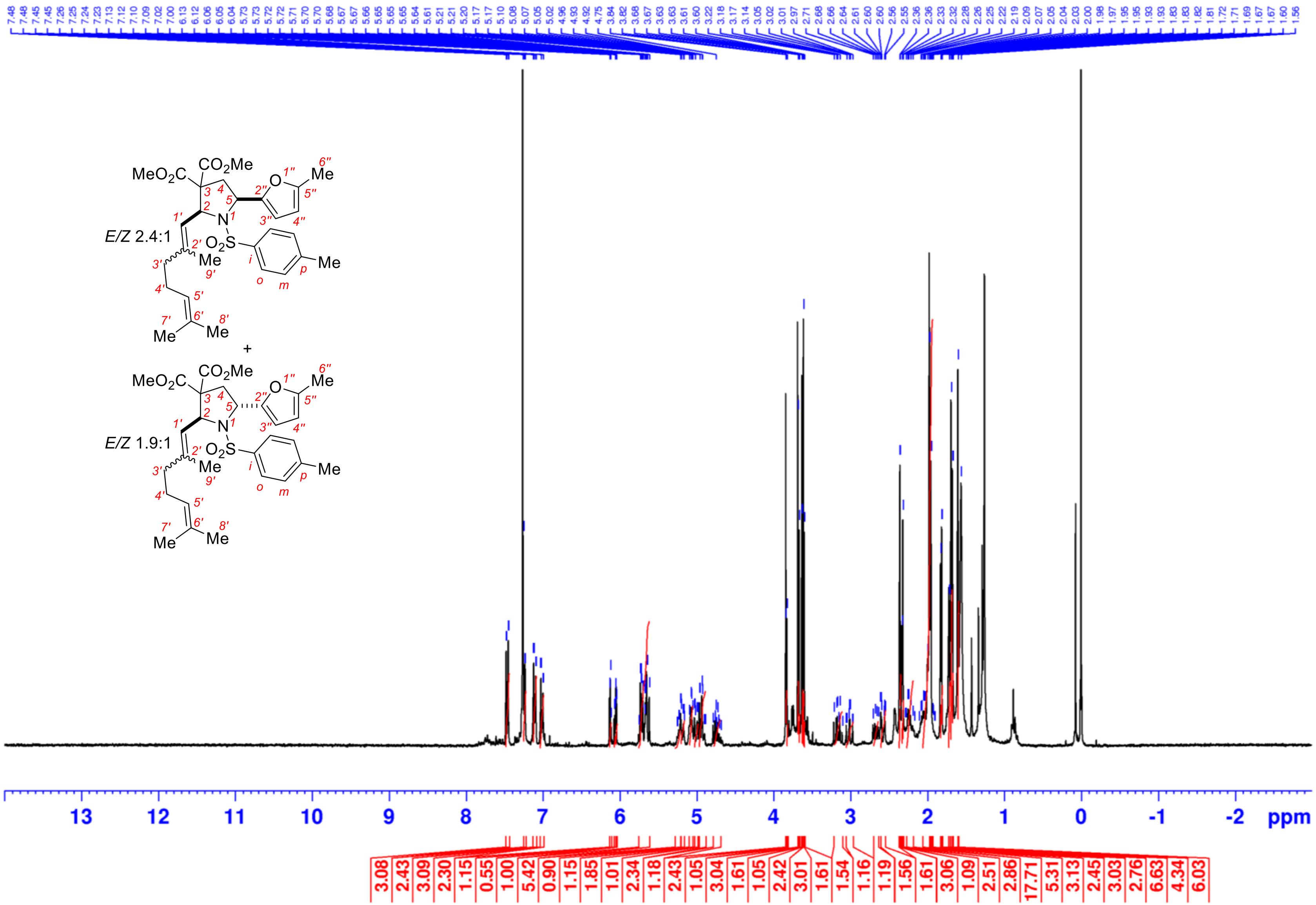


$^{1}H,^{13}C$-edited-HSQC NMR spectrum of **6c**, *trans* (*E/Z* 1.7:1)/*cis* (*E/Z* 1.7:1) 3.5:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

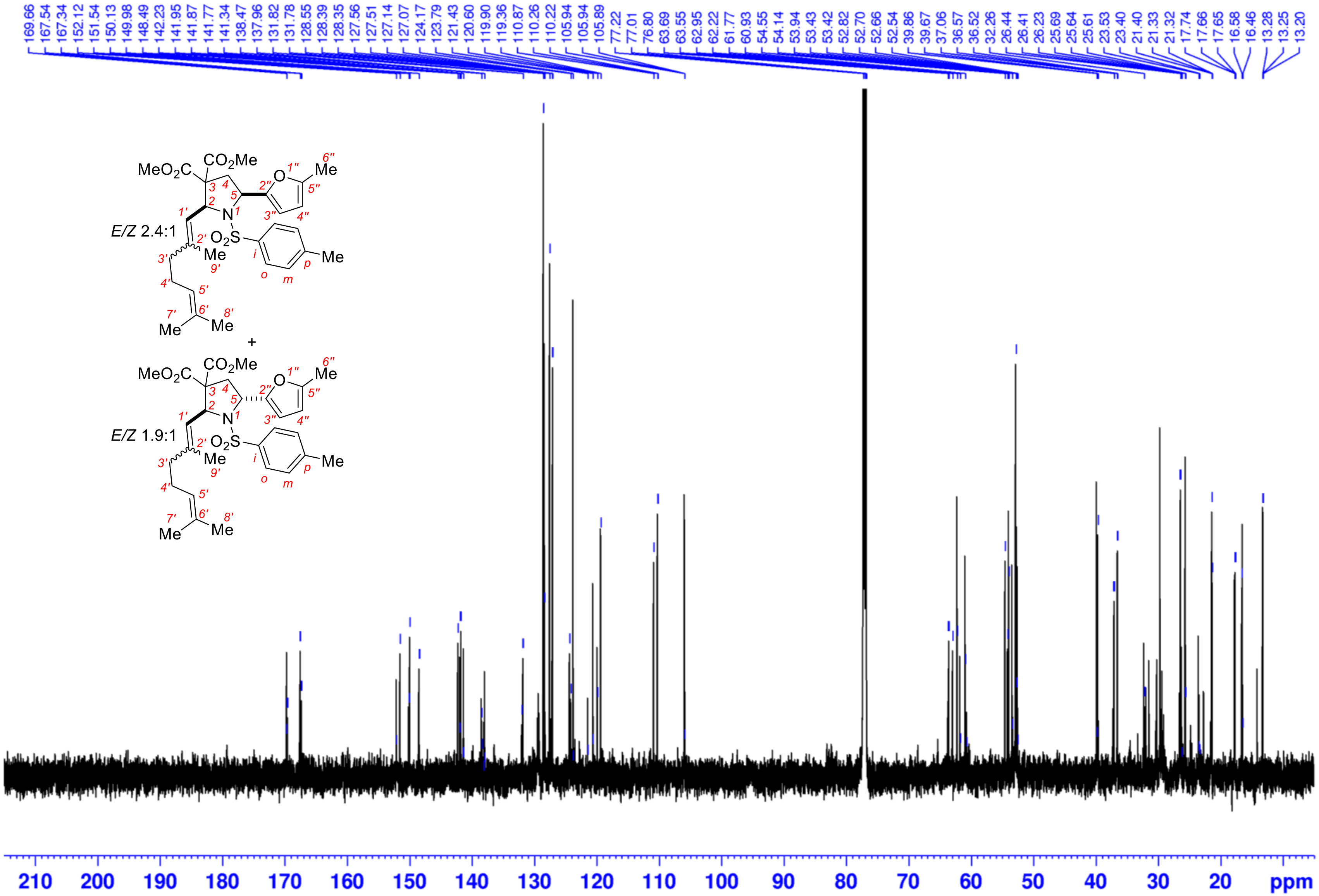


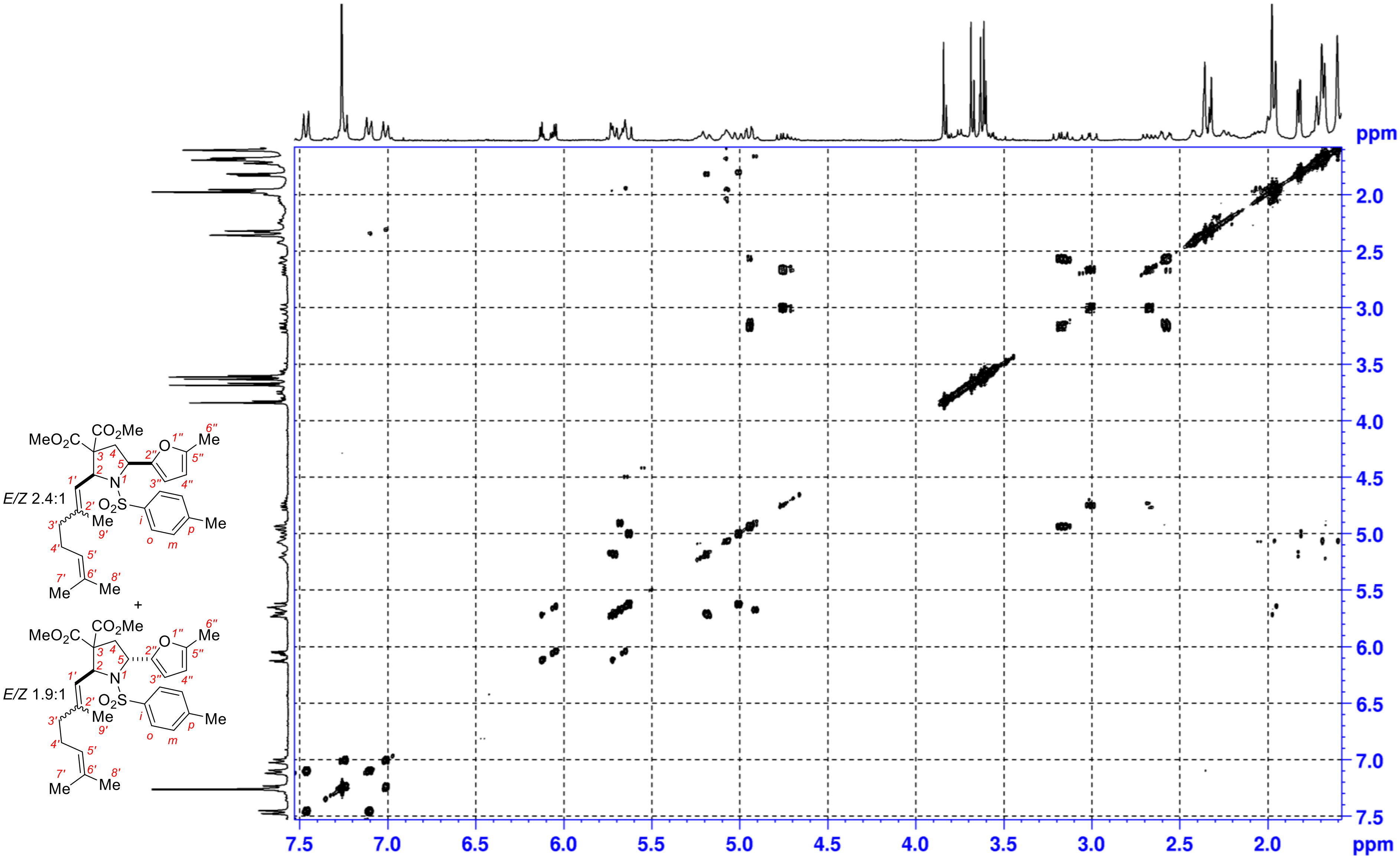

$^{1}H,^{13}C$-HMBC NMR spectrum of **6c**, *trans* (*E/Z* 1.7:1)/*cis* (*E/Z* 1.7:1) 3.5:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)



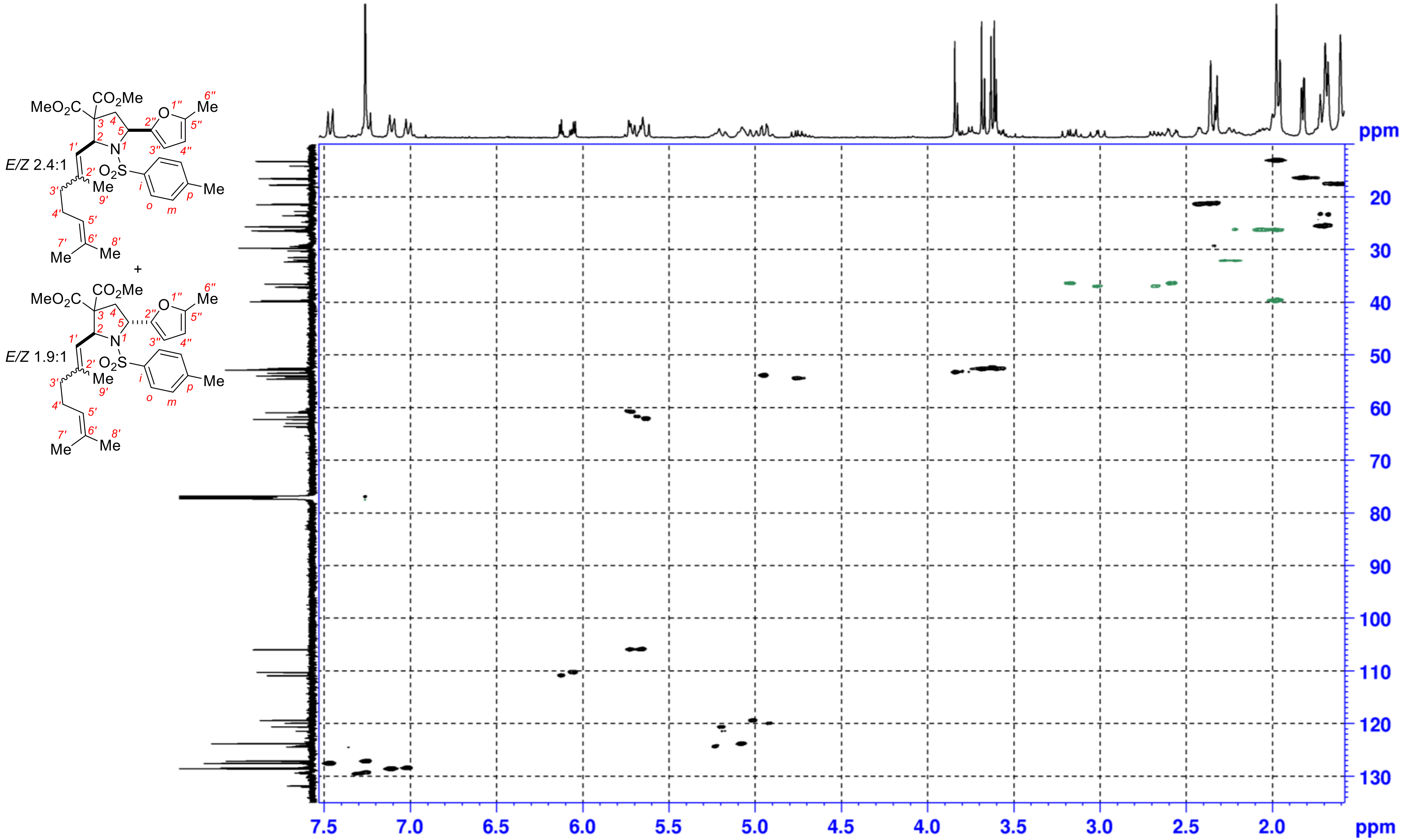
[1]H NMR spectrum of **6e**, *cis* (*E/Z* 2.4:1)/*trans* (*E/Z* 1.9:1) 1.3:1 (600.1 MHz, $CDCl_3$)



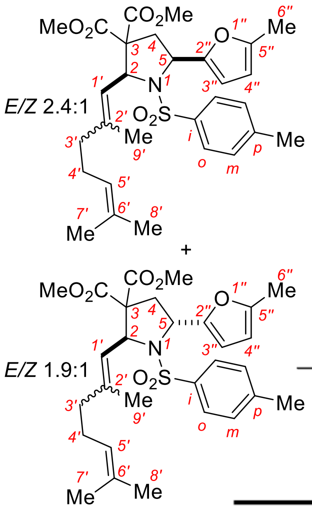

$^{13}$C NMR spectrum of **6e**, *cis* (*E/Z* 2.4:1)/*trans* (*E/Z* 1.9:1) 1.3:1 (150.9 MHz, $CDCl_3$)

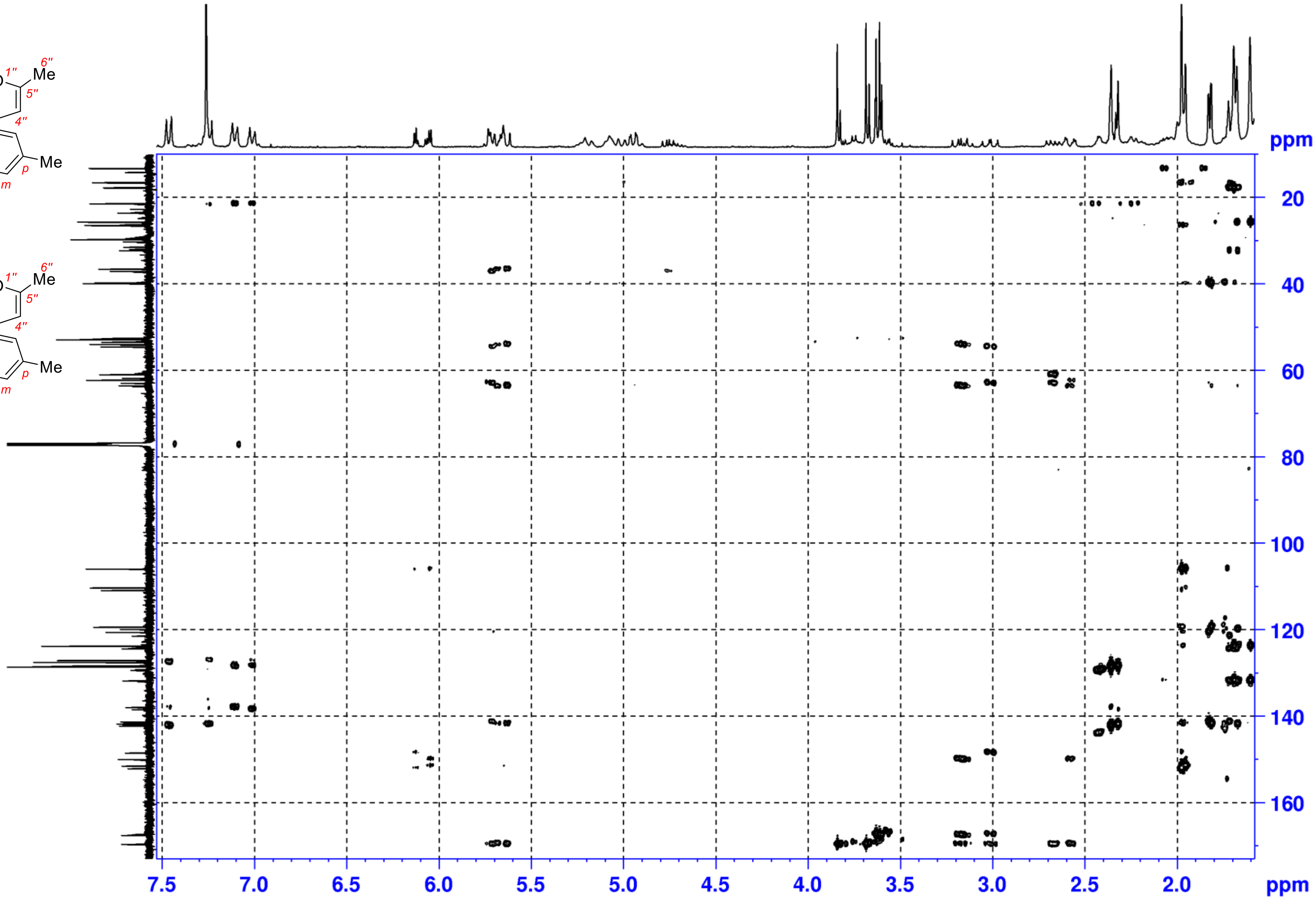


$^{1}H,^{1}H$-COSY NMR spectrum of **6e**, *cis* (*E/Z* 2.4:1)/*trans* (*E/Z* 1.9:1) 1.3:1 (600.1 MHz, $CDCl_3$)

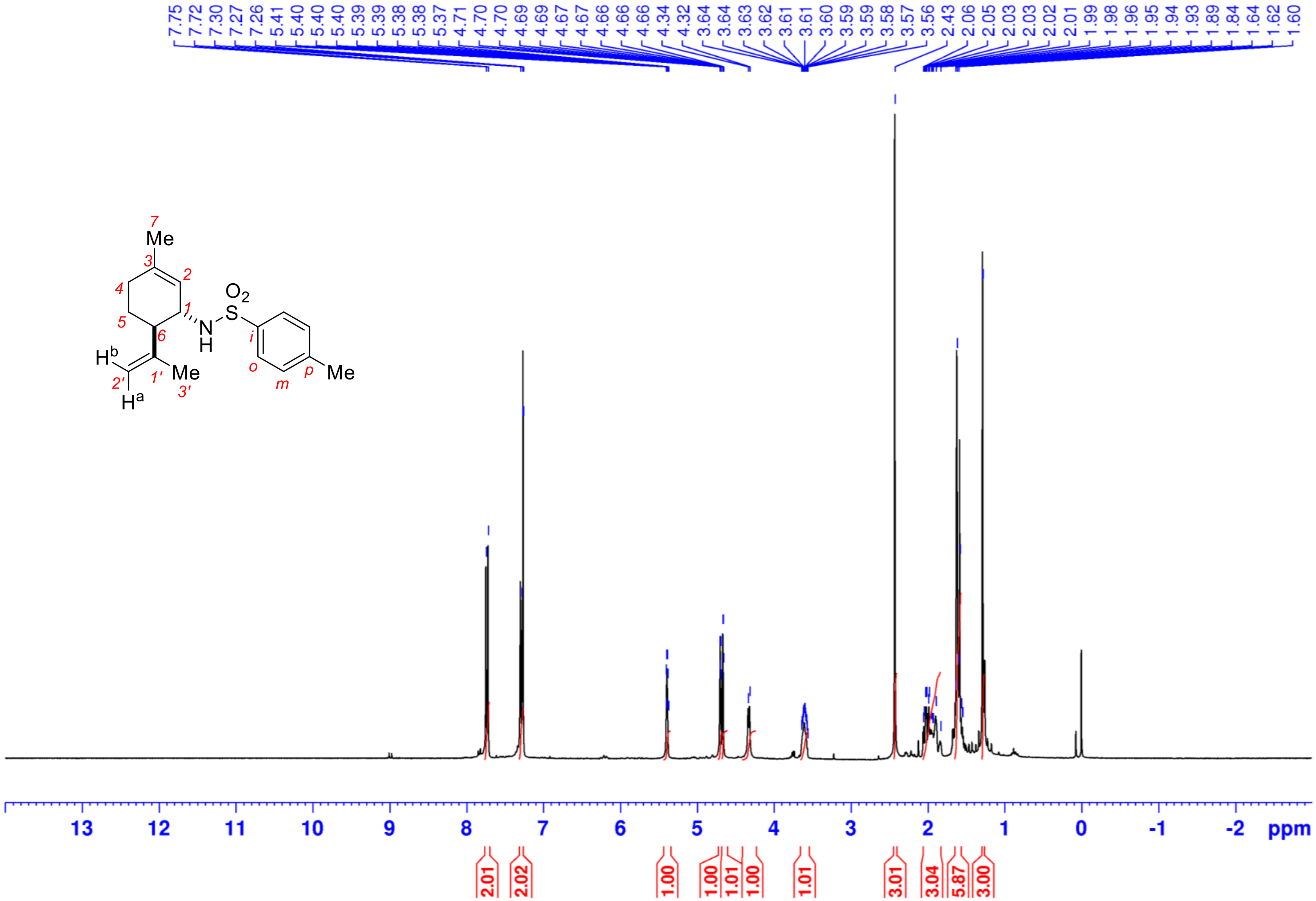



$^{1}$H,$^{13}$C-edited-HSQC NMR spectrum of **6e**, *cis* (*E/Z* 2.4:1)/*trans* (*E/Z* 1.9:1) 1.3:1 ($^{1}$H: 600.1 MHz; $^{13}$C: 150.9 MHz; $CDCl_3$)

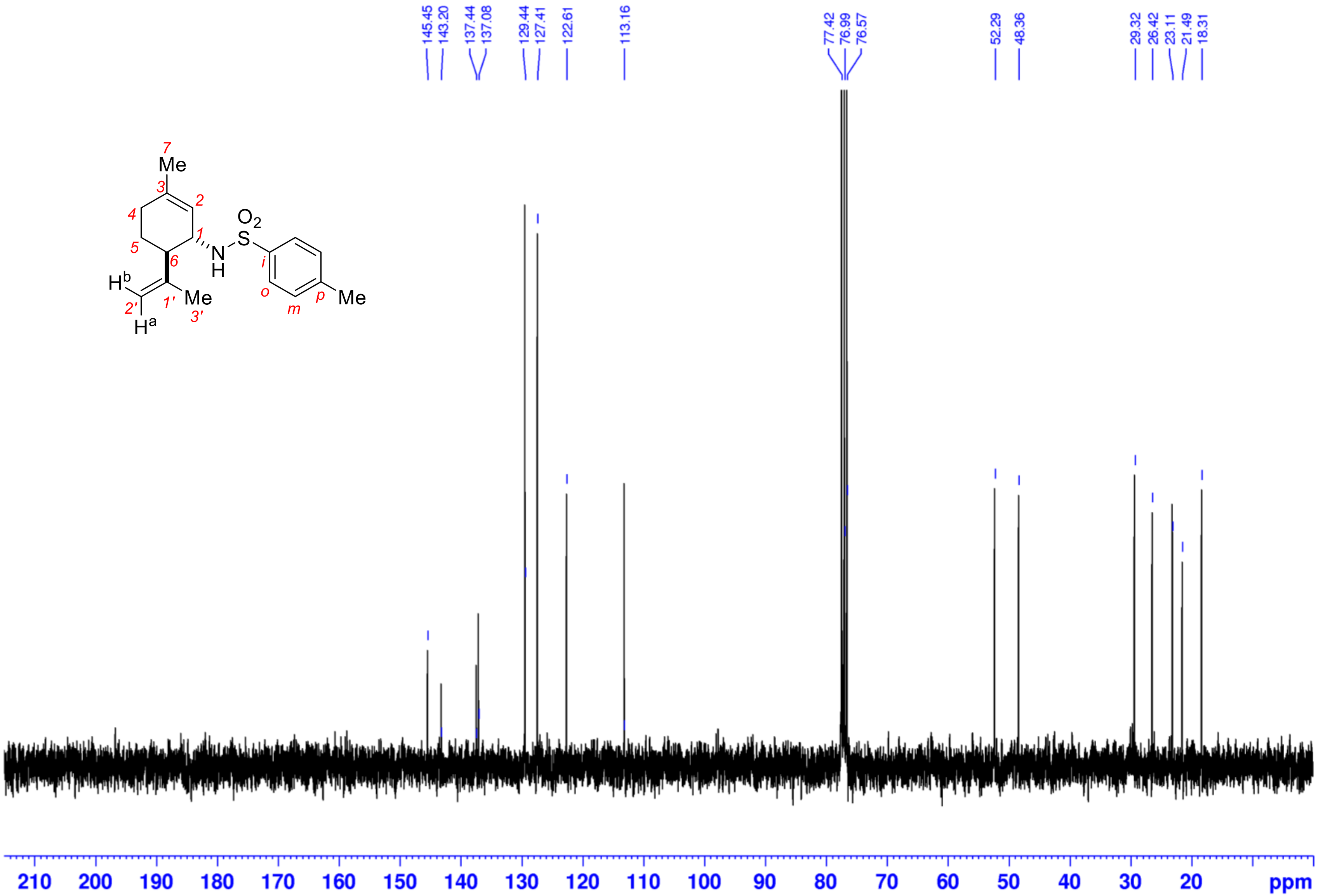


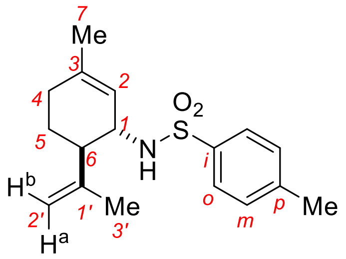

$^{1}$H,$^{13}$C-HMBC NMR spectrum of **6e**, *cis* (*E/Z* 2.4:1)/*trans* (*E/Z* 1.9:1) 1.3:1 ($^{1}$H: 600.1 MHz; $^{13}$C: 150.9 MHz; $CDCl_3$)

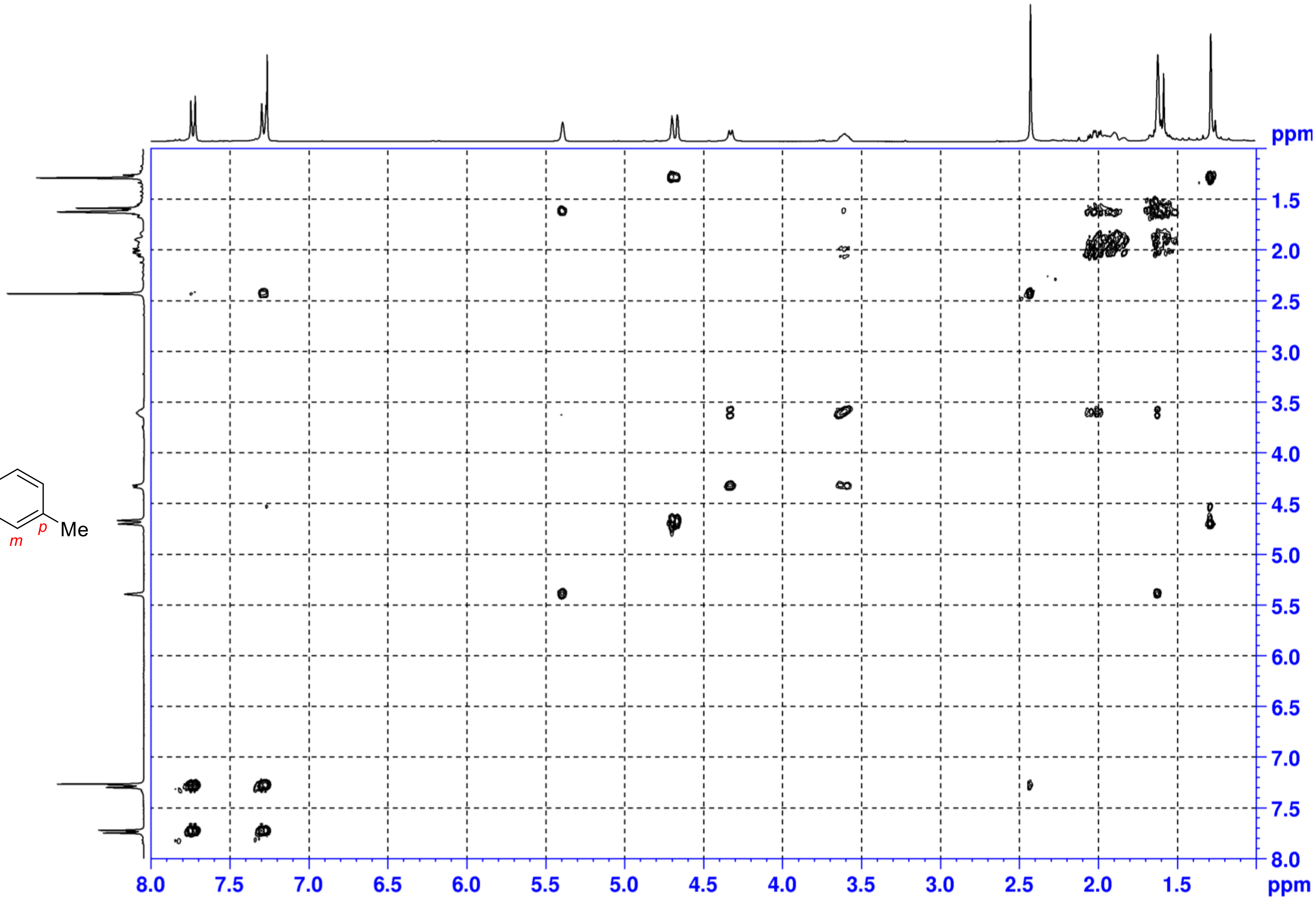



$^{1}$H NMR spectrum of **8** (300.1 MHz, $CDCl_3$)

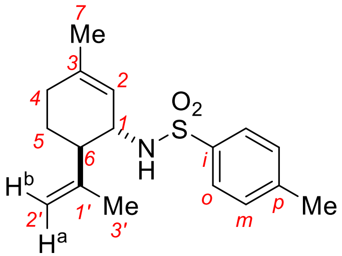


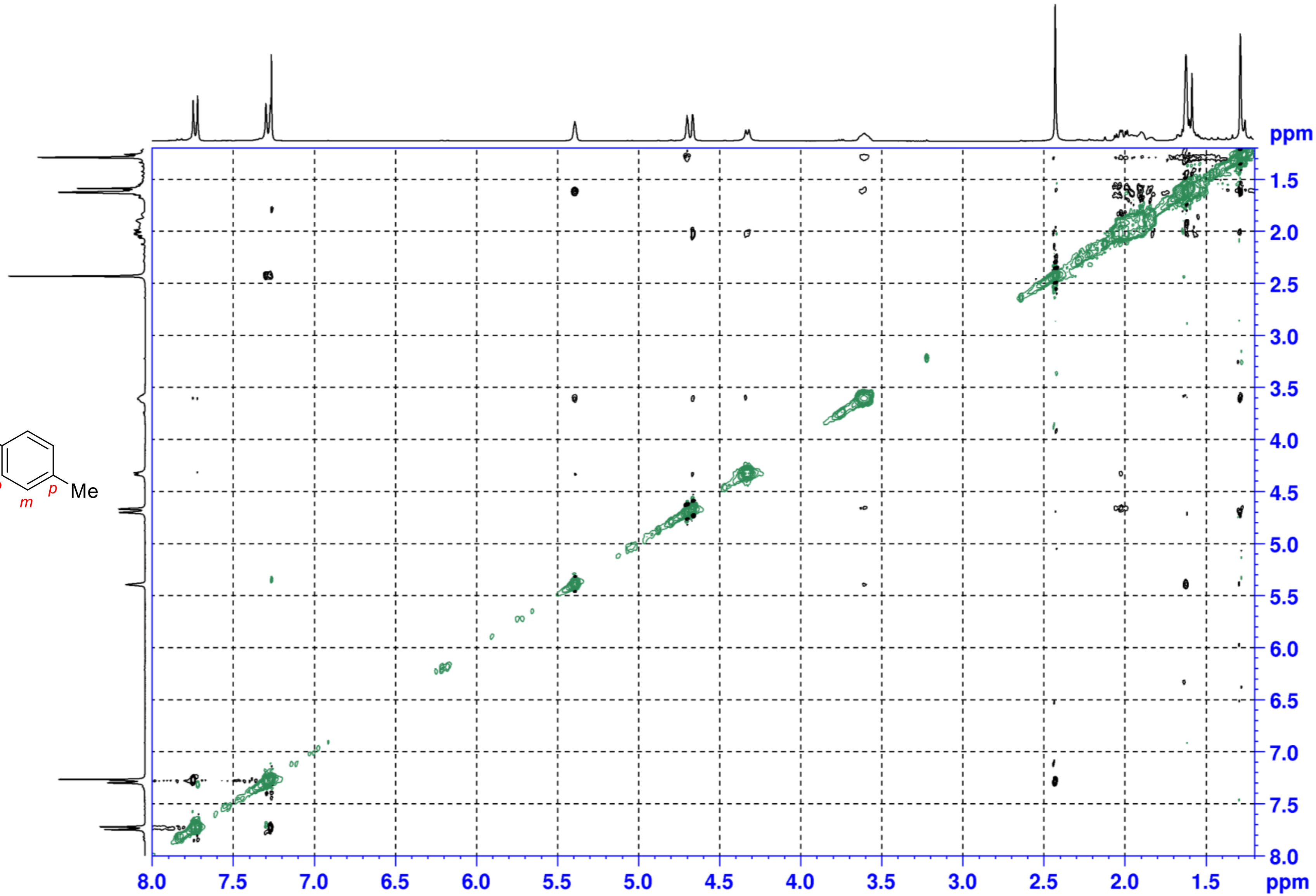

$^{13}$C NMR spectrum of **8** (75.5 MHz, $CDCl_3$)



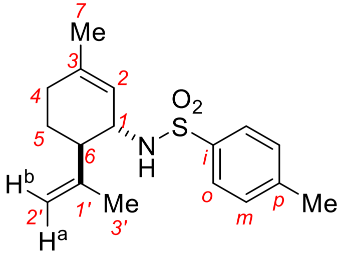



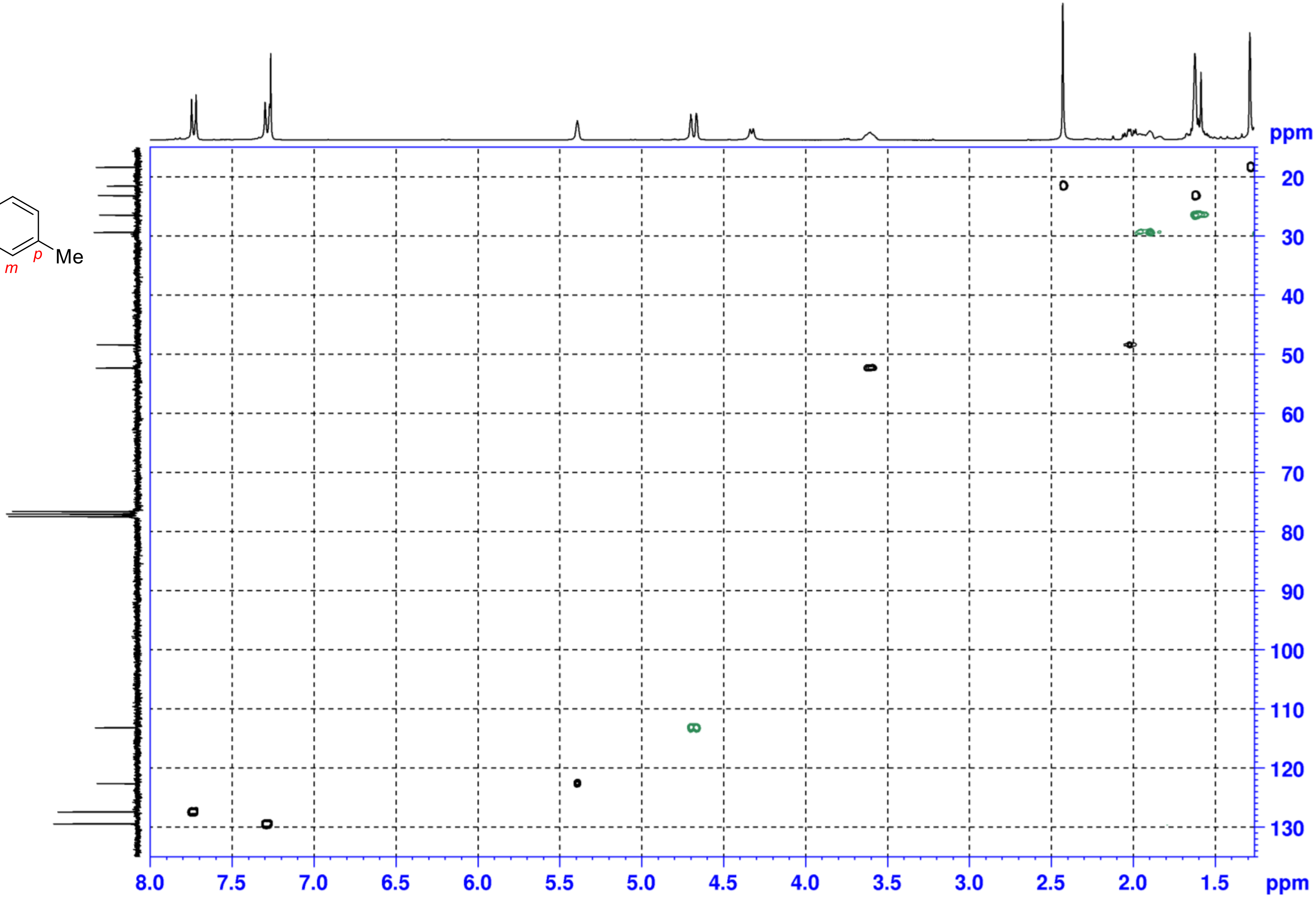

[1]H,[1]H-COSY NMR spectrum of **8** (300.1 MHz, $CDCl_3$)



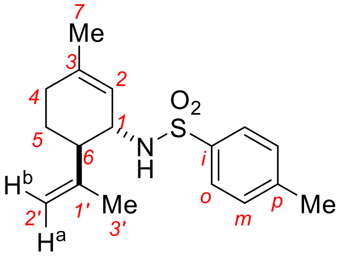



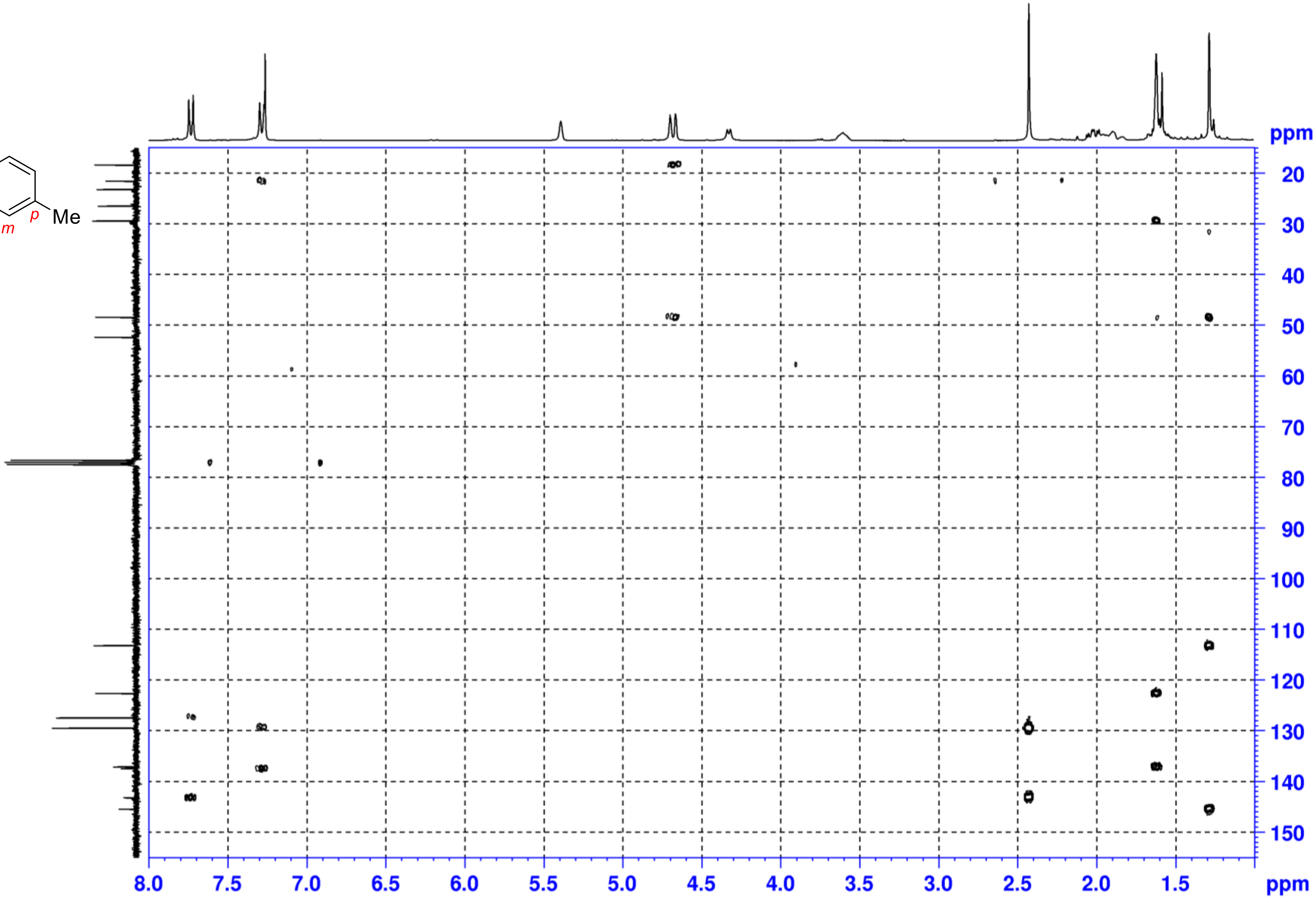

[1]H,[1]H-NOESY NMR spectrum of **8** (300.1 MHz, $CDCl_3$)



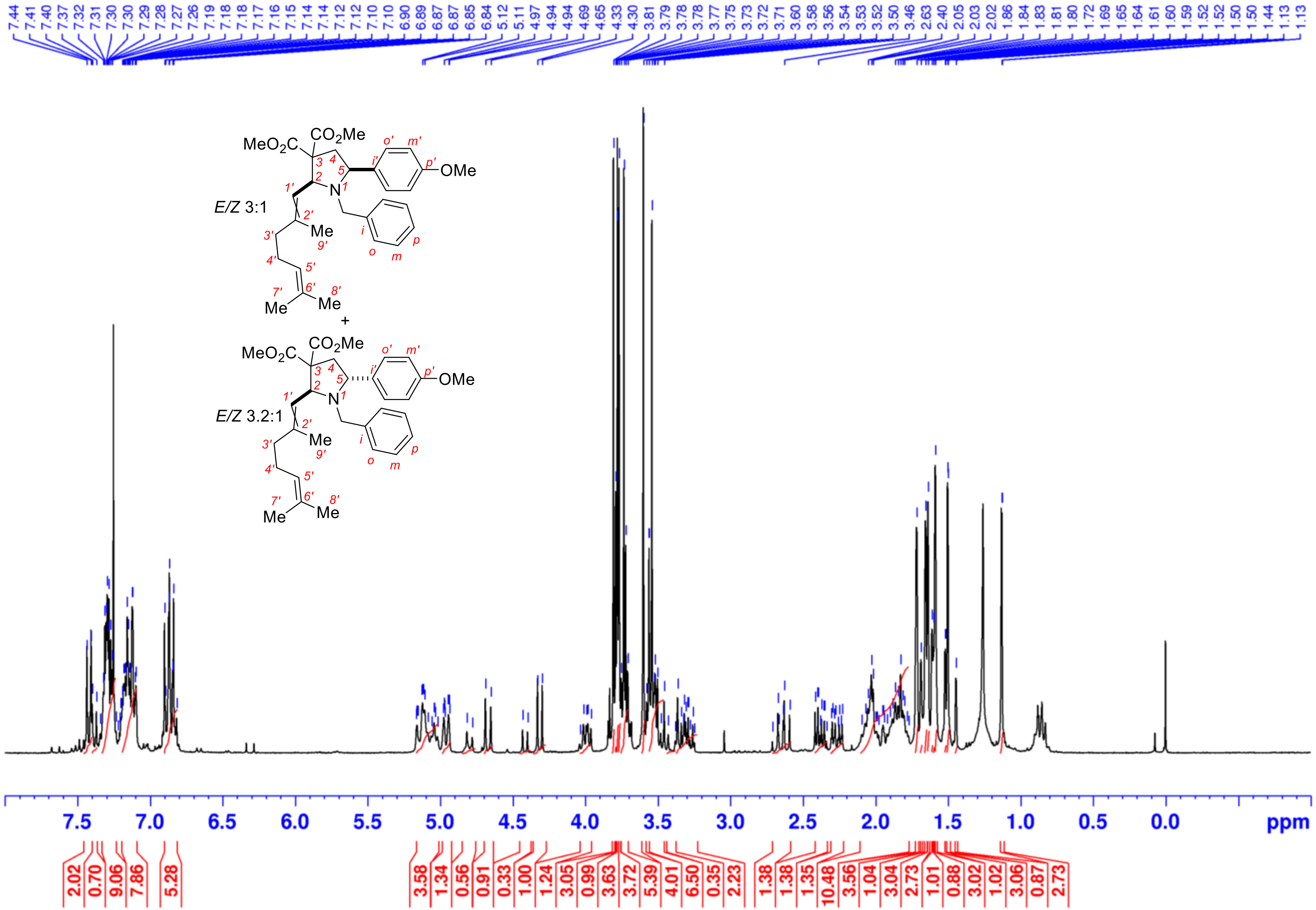




$^{1}H,^{13}C$-edited-HSQC NMR spectrum of **8** ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

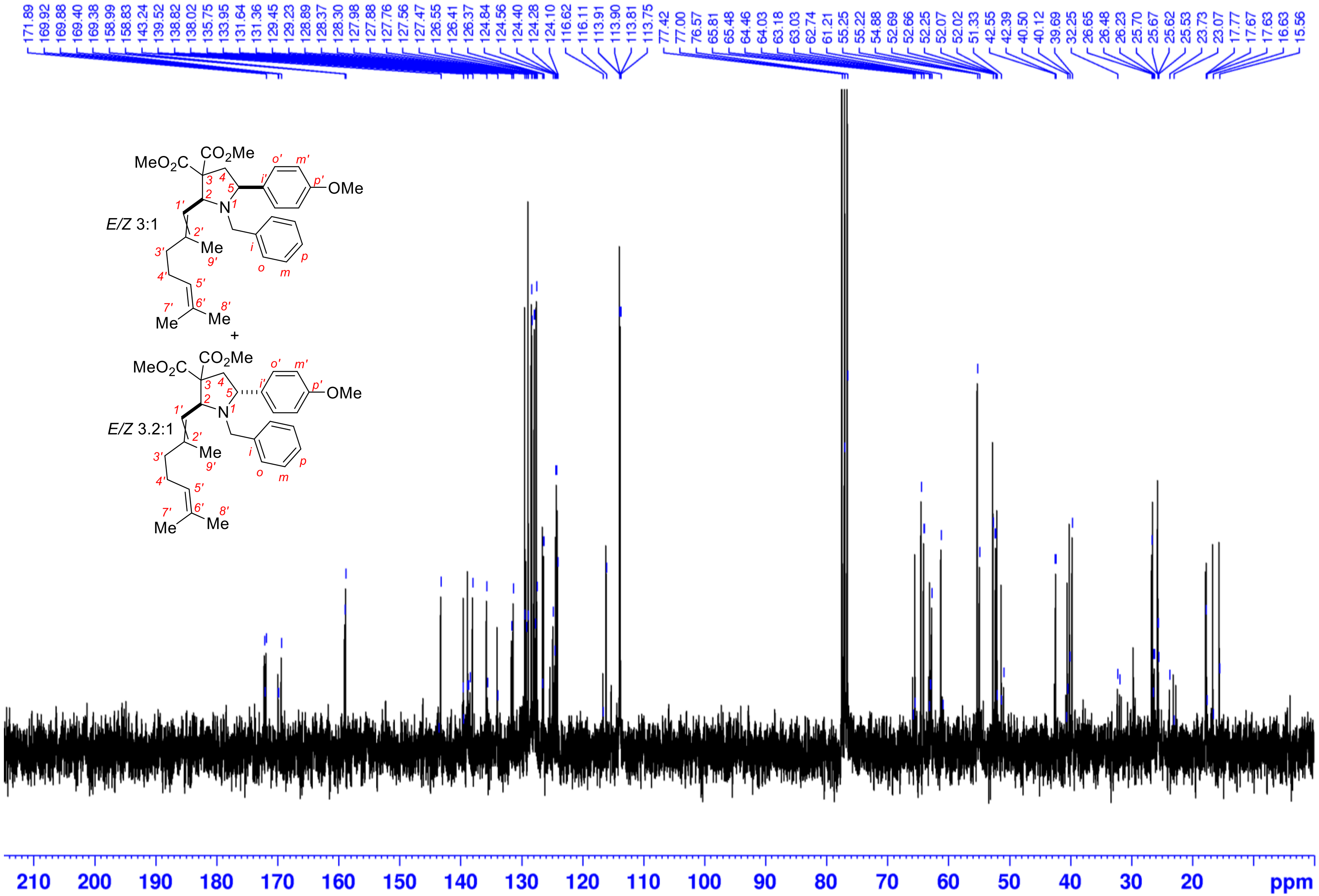


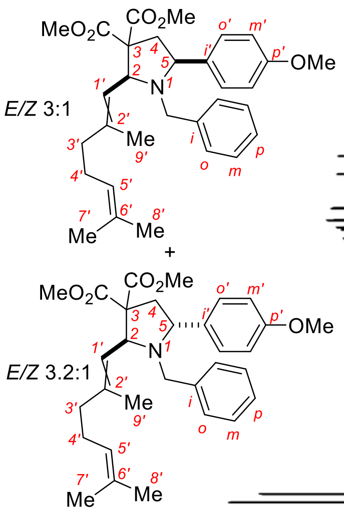

$^{1}H,^{13}C$-HMBC NMR spectrum of **8** ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

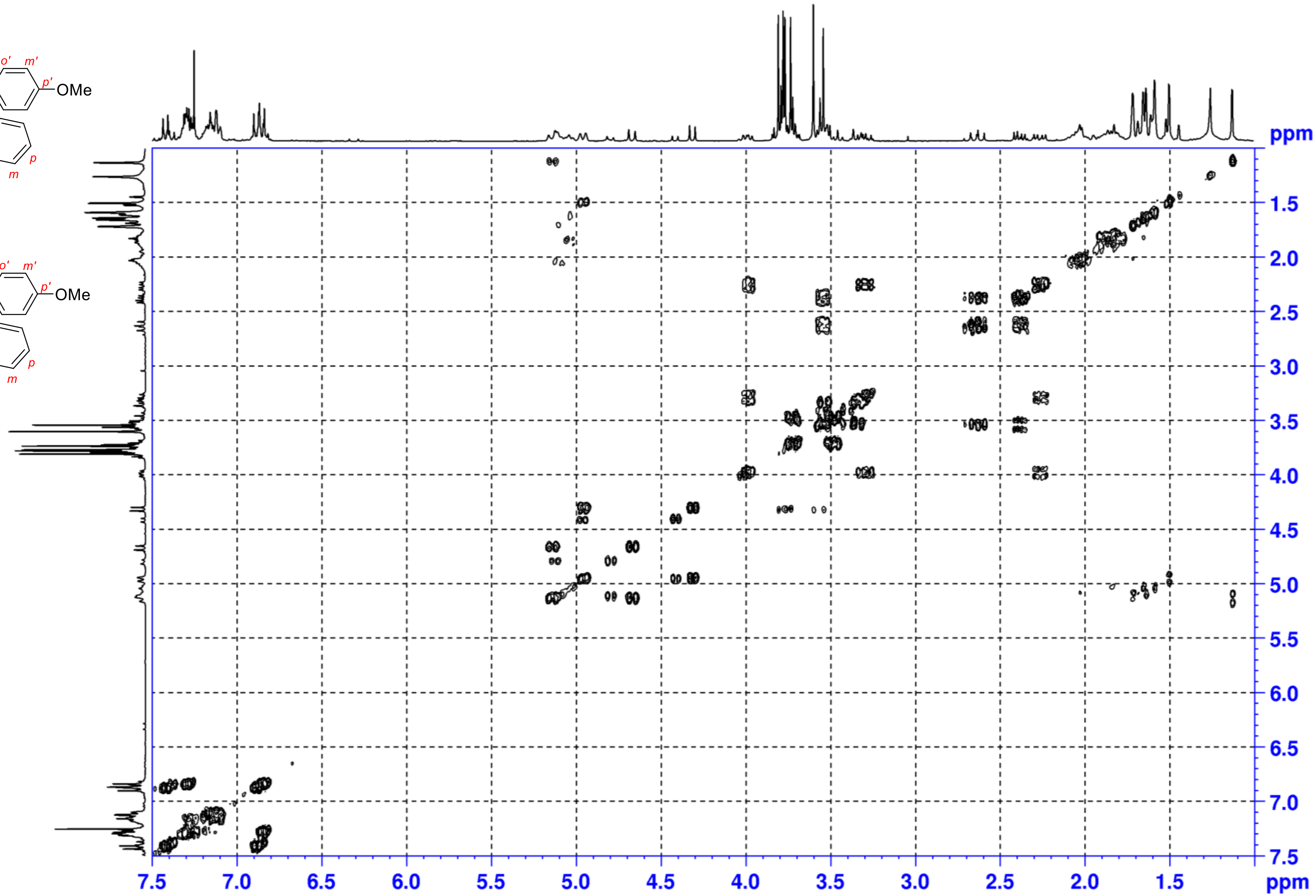


[1]H NMR spectrum of **9**, *cis* (*E/Z* 3:1)/*trans* (*E/Z* 3.2:1) 1.1:1 (300.1 MHz, $CDCl_3$)

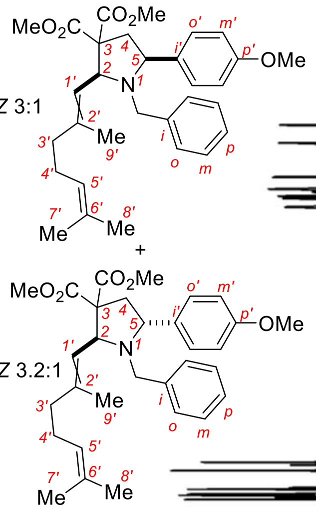


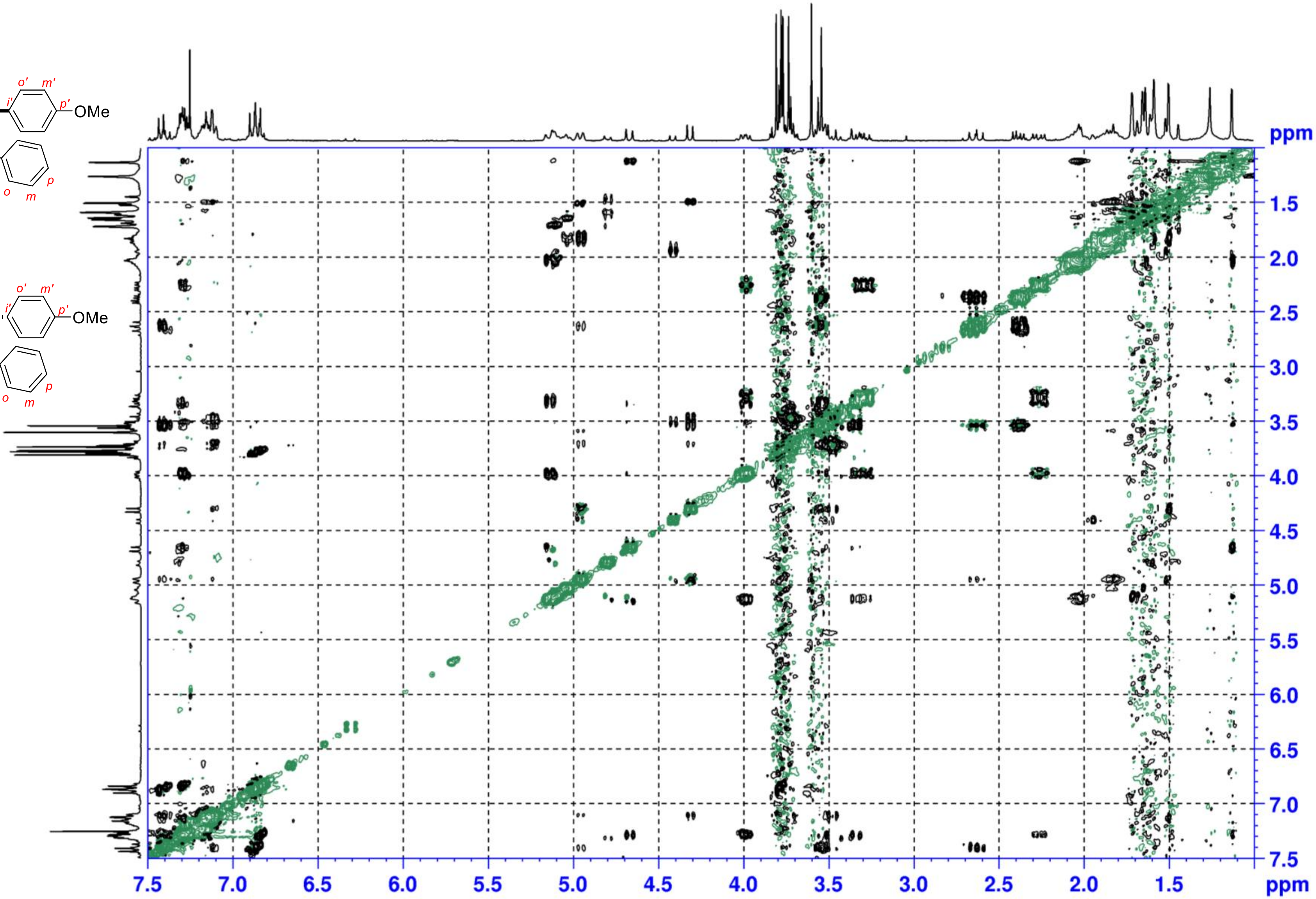
$^{13}$C NMR spectrum of **9**, *cis* (*E/Z* 3:1)/*trans* (*E/Z* 3.2:1) 1.1:1 (75.5 MHz, $CDCl_3$)



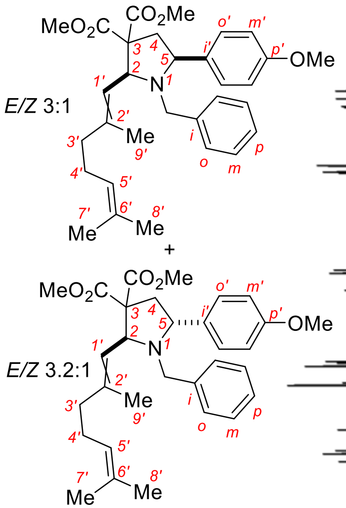



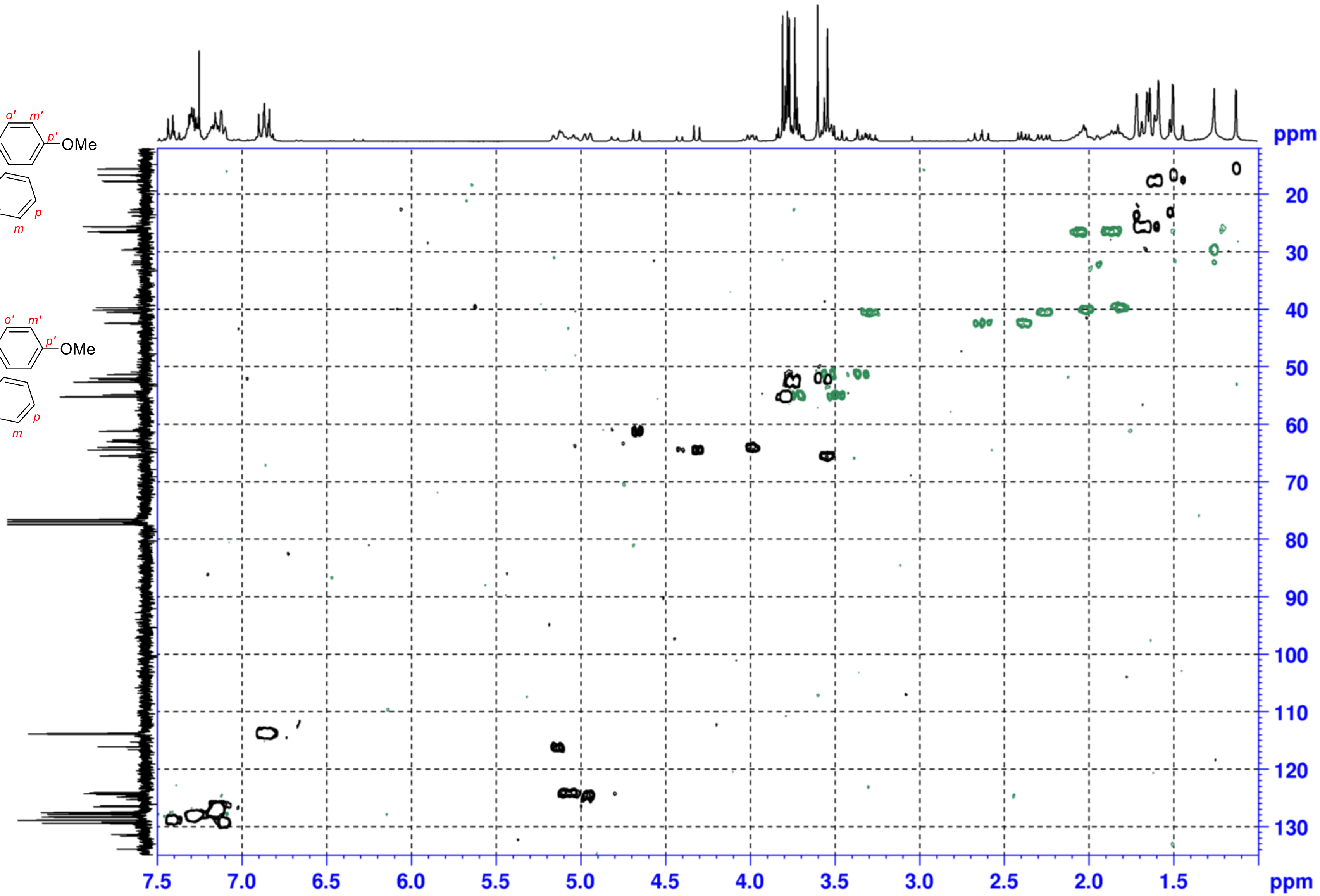
[1]H,[1]H-COSY NMR spectrum of **9**, *cis* (*E/Z* 3:1)/*trans* (*E/Z* 3.2:1) 1.1:1 (300.1 MHz, $CDCl_3$)



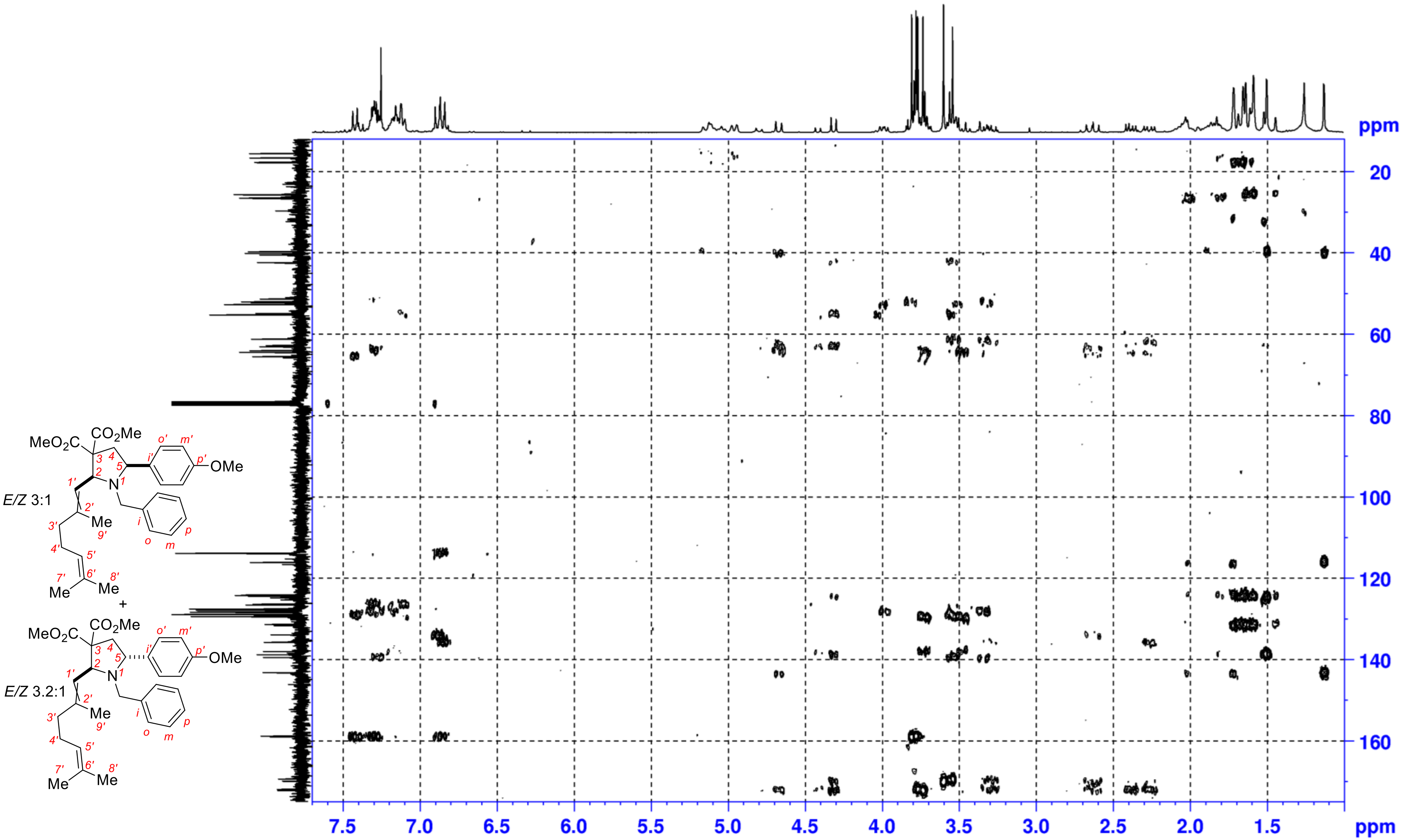




$^{1}H,^{1}H$-NOESY NMR spectrum of **9**, *cis* (*E/Z* 3:1)/*trans* (*E/Z* 3.2:1) 1.1:1 (300.1 MHz, $CDCl_3$)

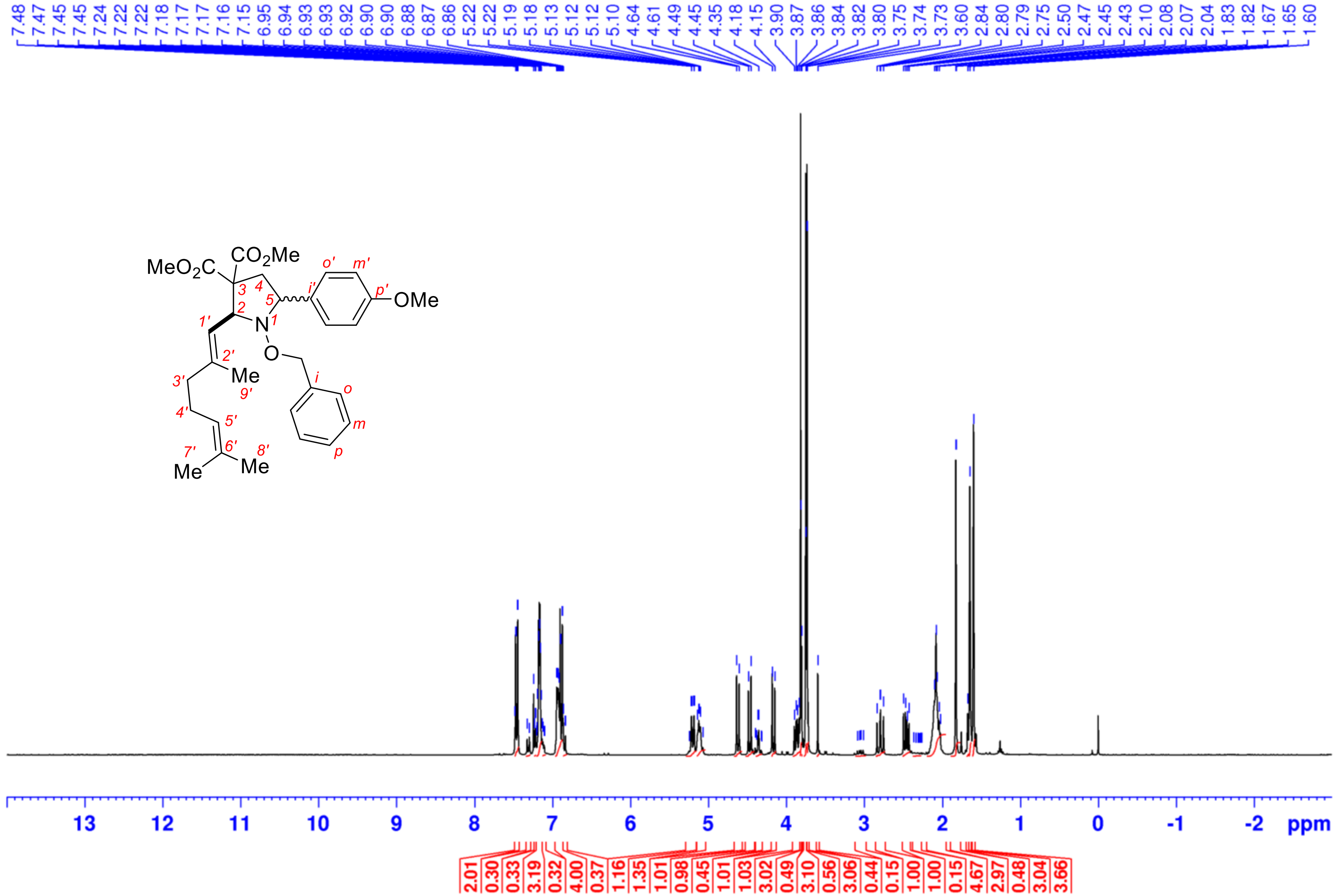




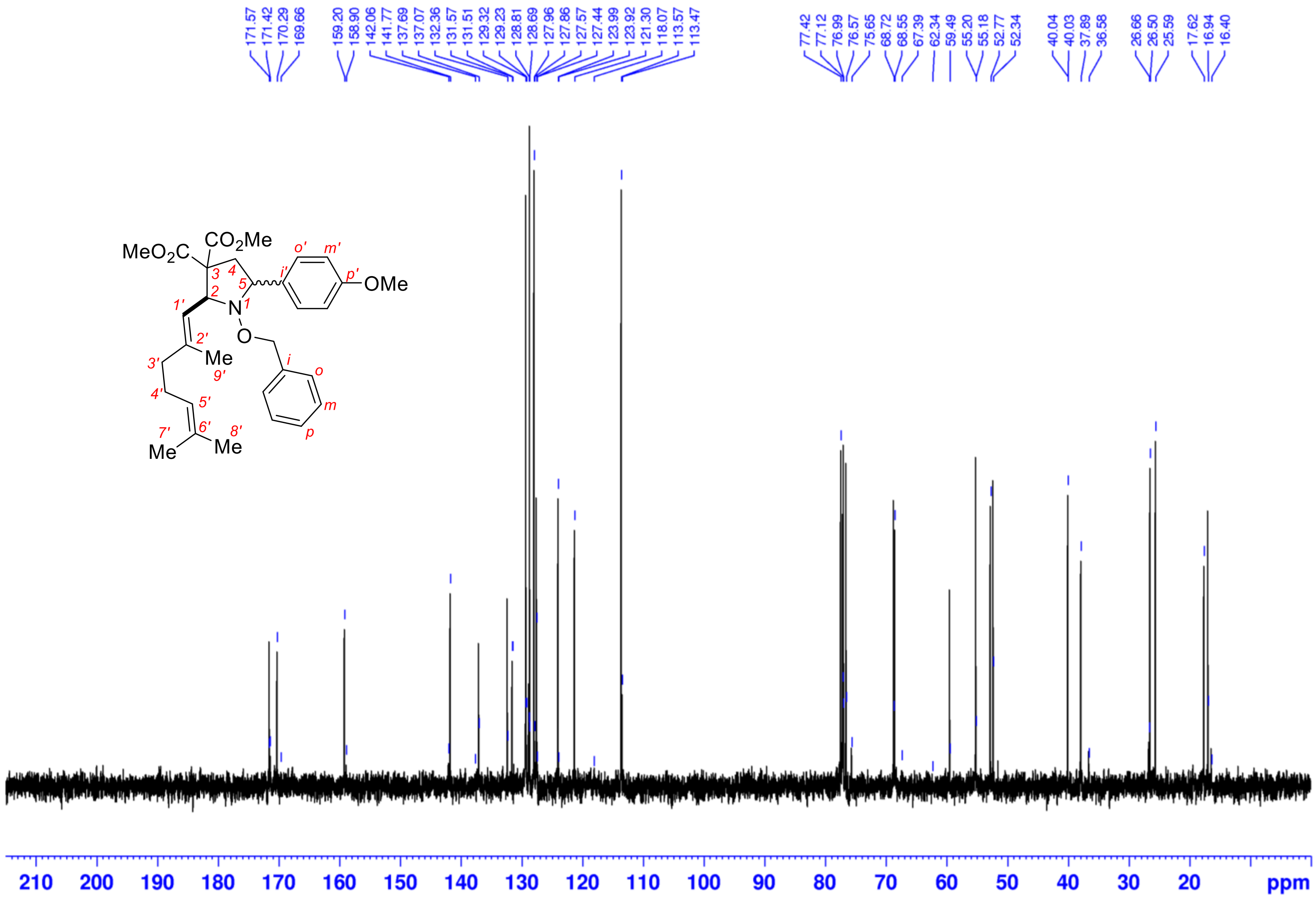
$^{1}H,^{13}C$-edited-HSQC NMR spectrum of **9**, *cis* (*E/Z* 3:1)/*trans* (*E/Z* 3.2:1) 1.1:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)



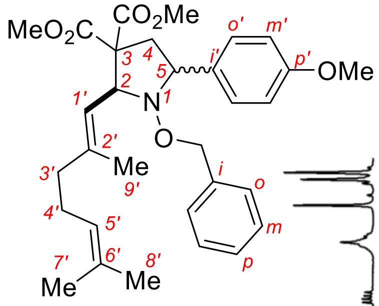

$^{1}H,^{13}C$-HMBC NMR spectrum of **9**, *cis* (*E*/*Z* 3:1)/*trans* (*E*/*Z* 3.2:1) 1.1:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

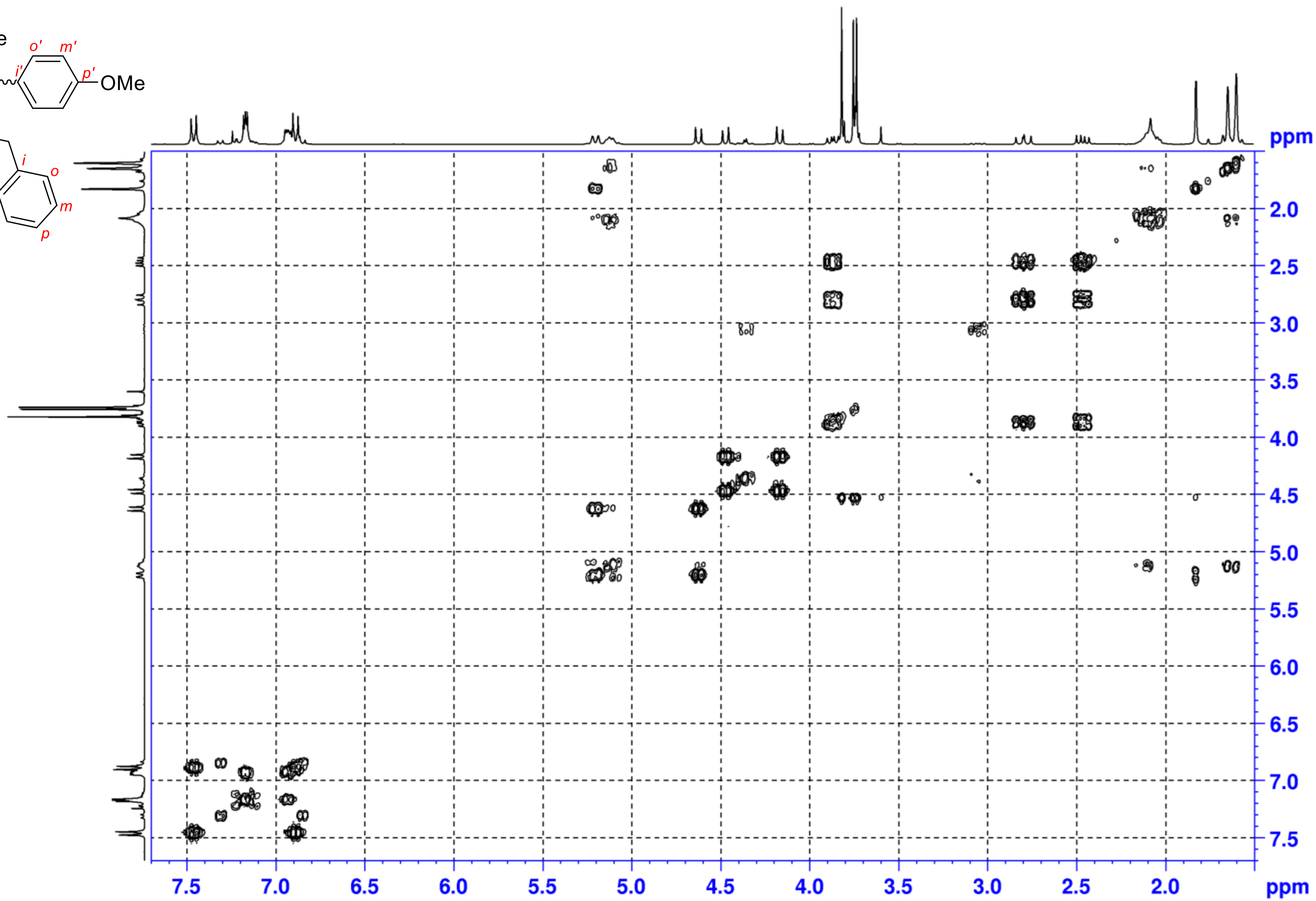


[1]H NMR spectrum of *E*-**10a**, *cis*/*trans* 6.7:1 (300.1 MHz, $CDCl_3$)

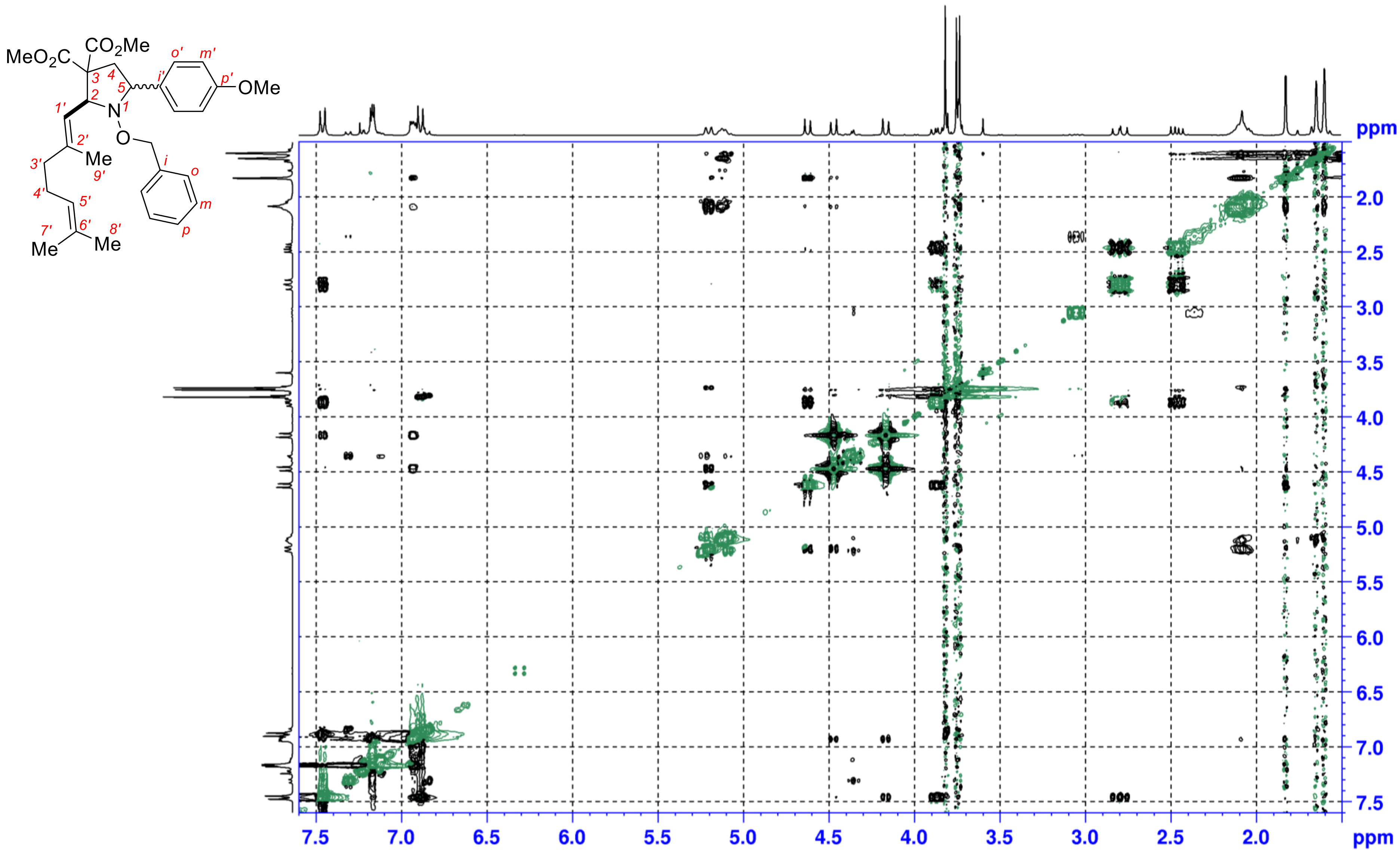



$^{13}$C NMR spectrum of *E*-**10a**, *cis*/*trans* 6.7:1 (75.5 MHz, $CDCl_3$)

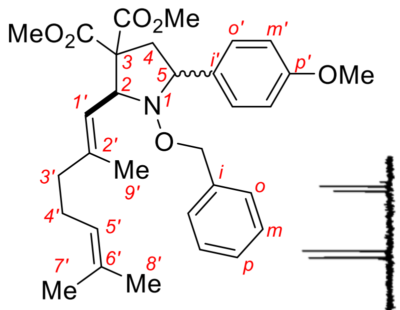


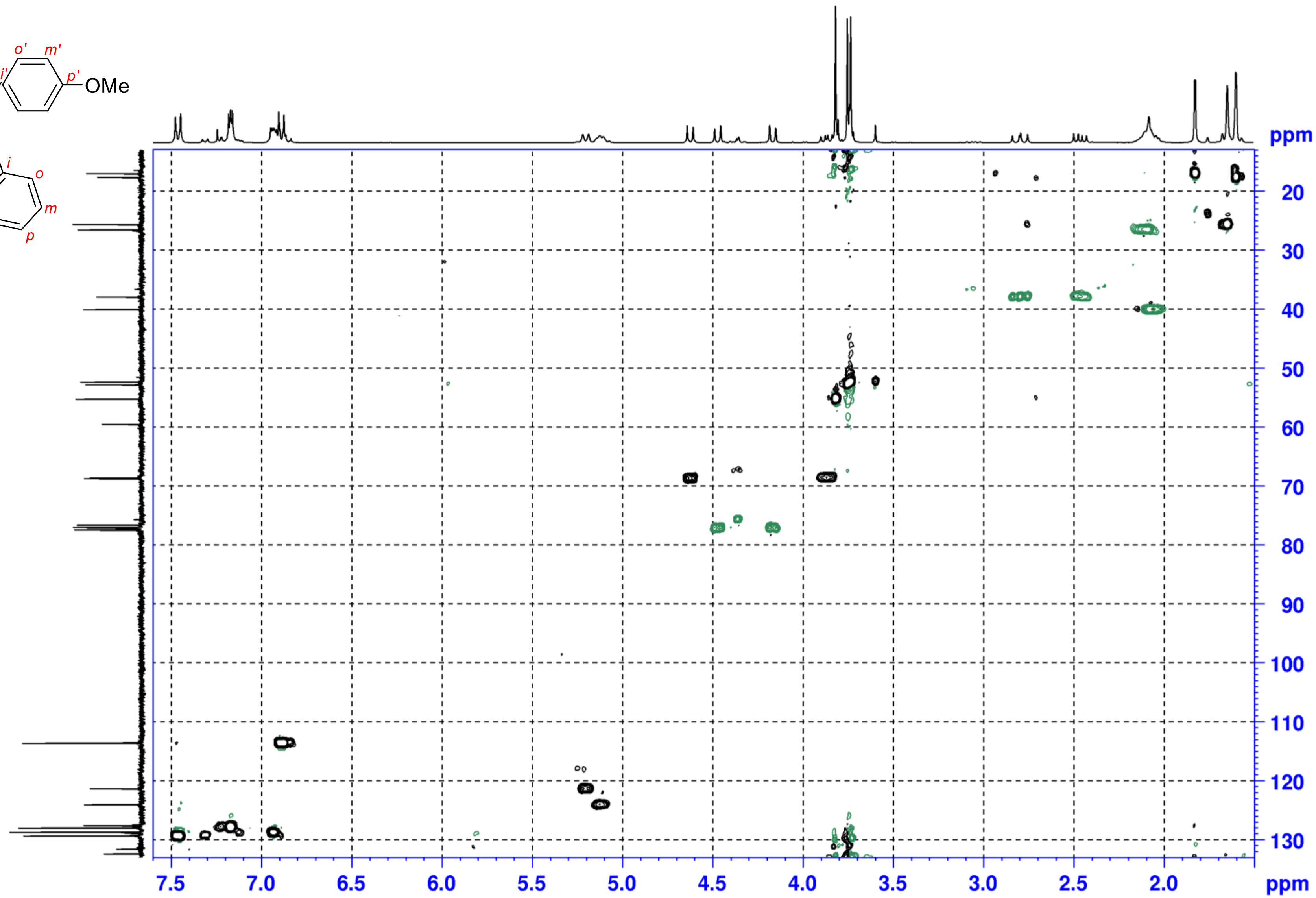



$^{1}H,^{1}H$-COSY NMR spectrum of *E*-**10a**, *cis*/*trans* 6.7:1 (300.1 MHz, $CDCl_3$)

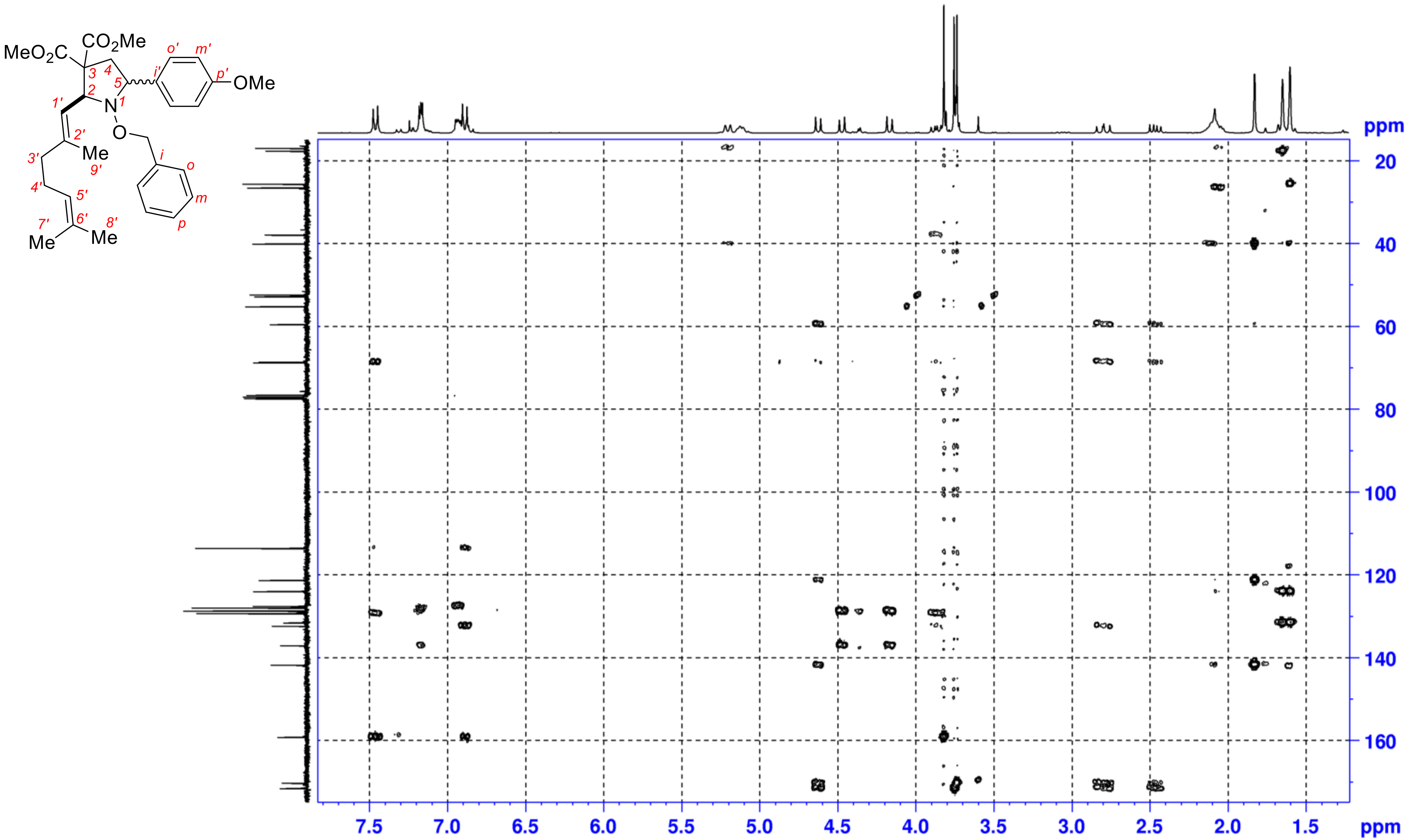



$^{1}$H,$^{1}$H-NOESY NMR spectrum of *E*-**10a**, *cis*/*trans* 6.7:1 (300.1 MHz, $CDCl_3$)

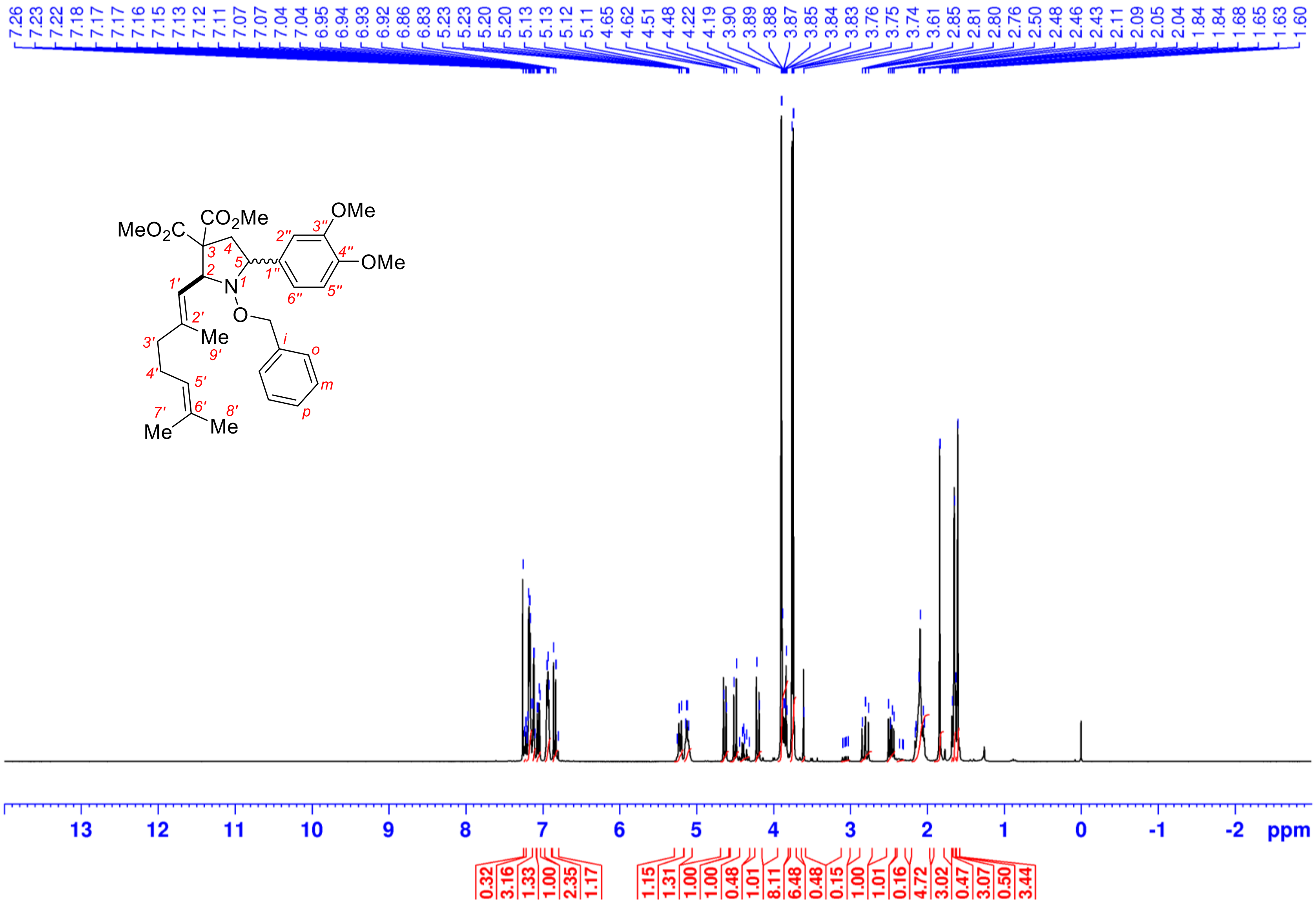


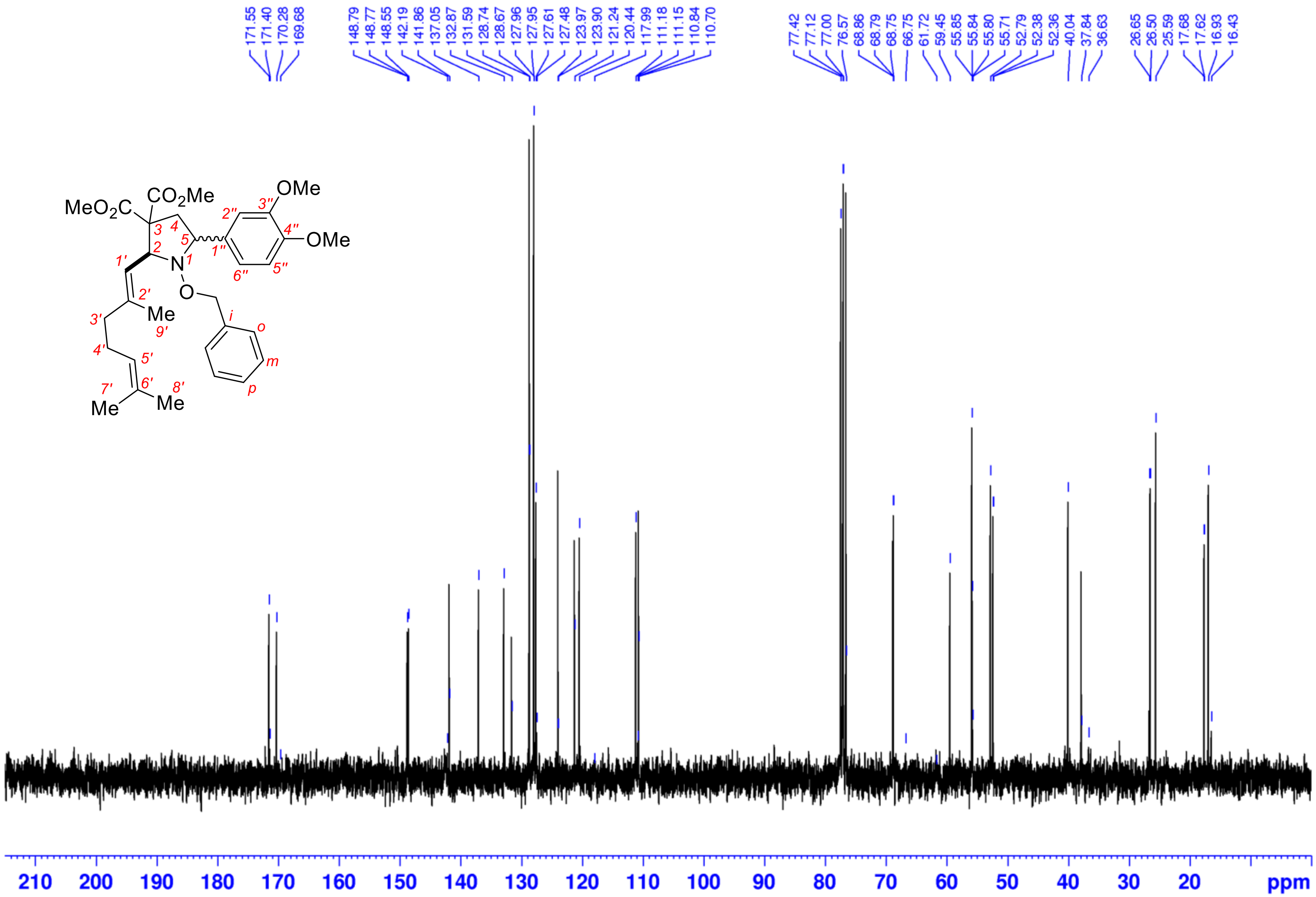

$^1H,^{13}C$-edited-HSQC NMR spectrum of *E*-**10a**, *cis*/*trans* 6.7:1 ($^1H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)



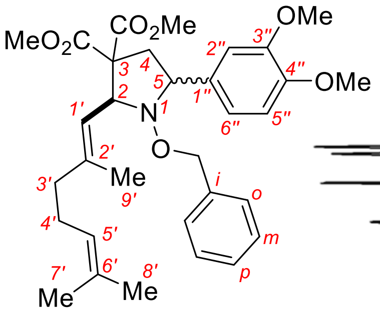

$^{1}$H,$^{13}$C-HMBC NMR spectrum of *E*-**10a**, *cis*/*trans* 6.7:1 ($^{1}$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)

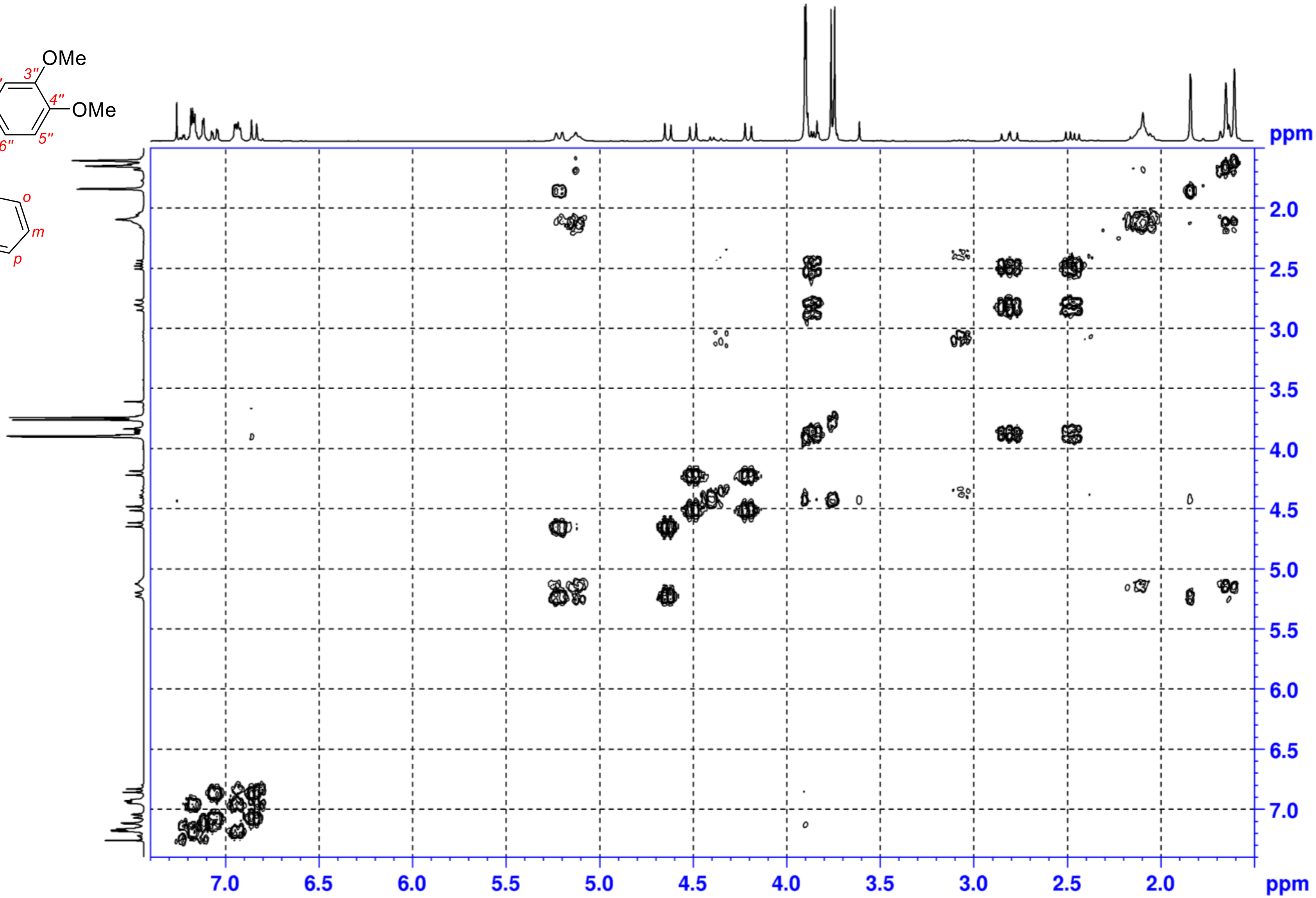



[1]H NMR spectrum of *E*-**10b**, *cis*/*trans* 6.7:1 (300.1 MHz, $CDCl_3$)

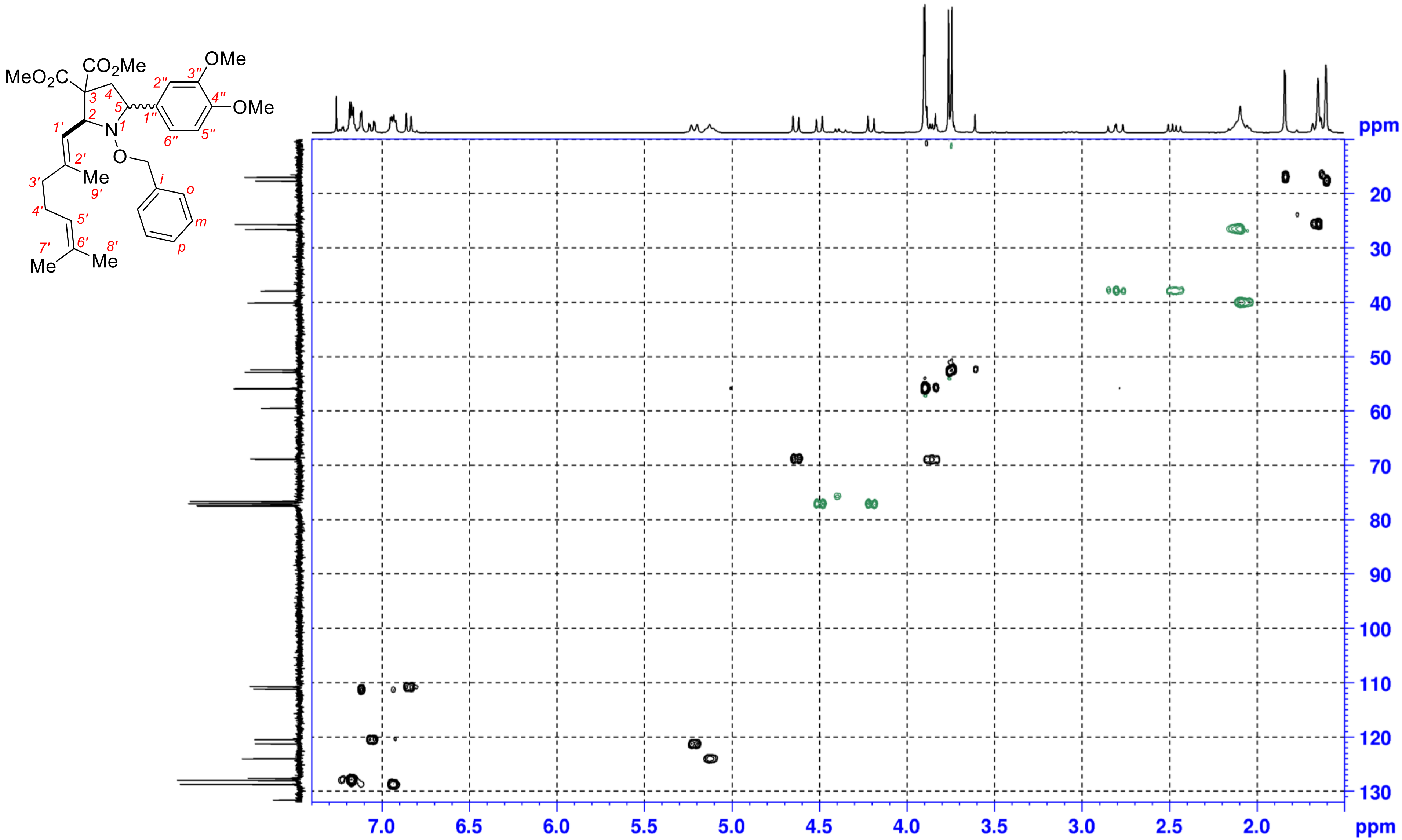


$^{13}$C NMR spectrum of *E*-**10b**, *cis*/*trans* 6.7:1 (75.5 MHz, $CDCl_3$)

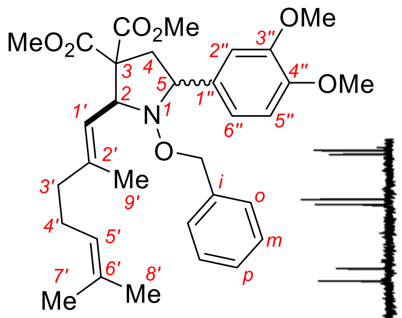


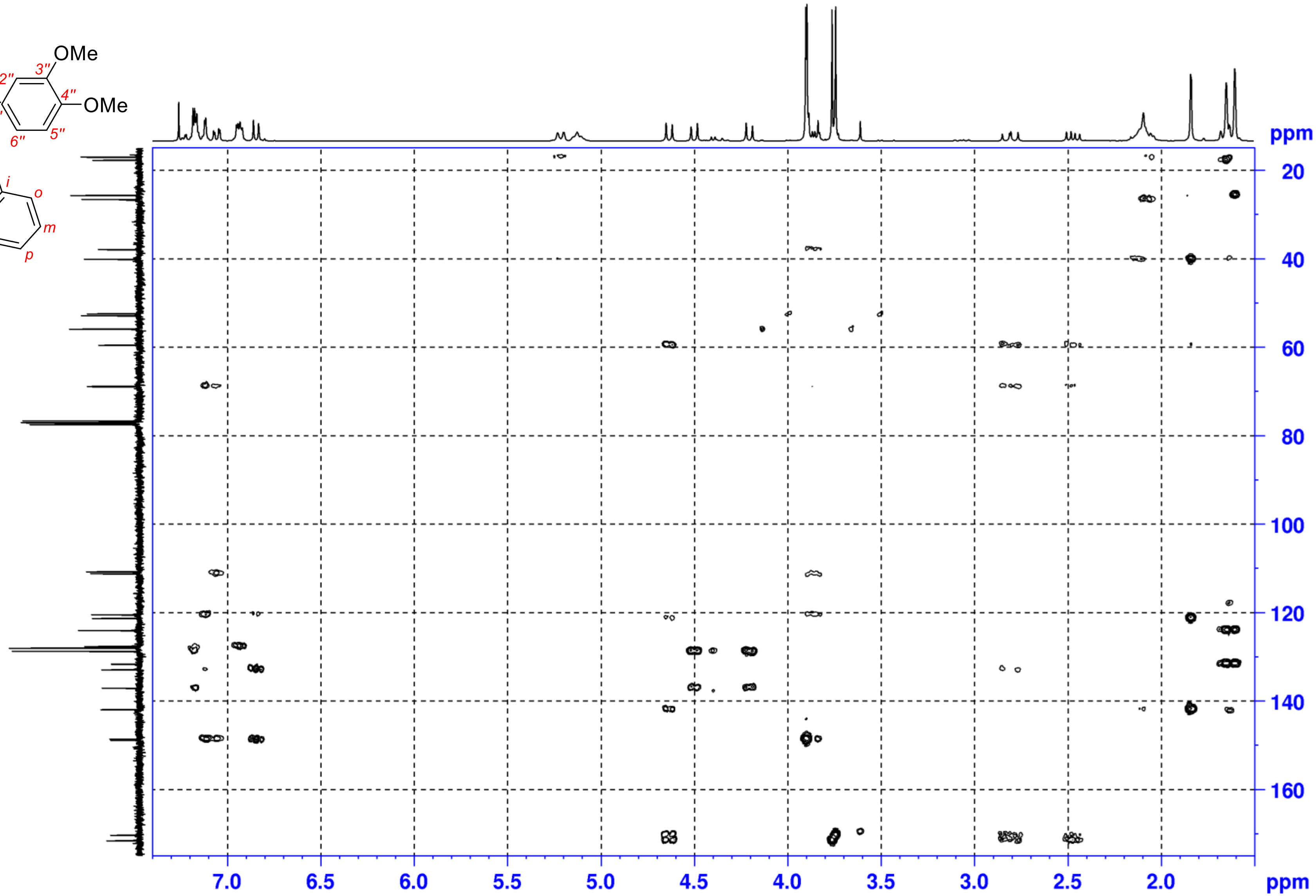




$^{1}H,^{1}H$-COSY NMR spectrum of *E*-**10b**, *cis*/*trans* 6.7:1 (300.1 MHz, $CDCl_3$)

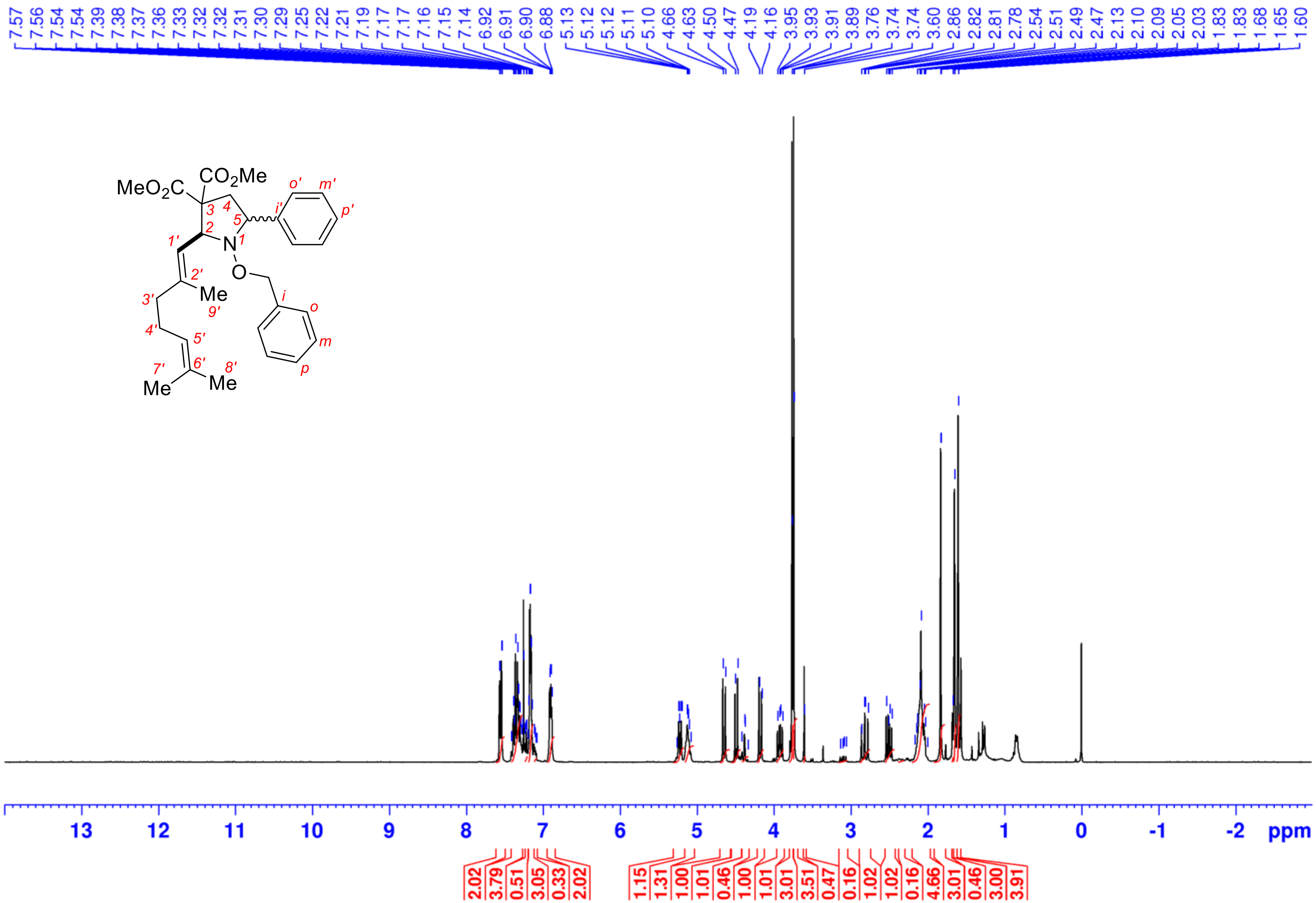



[1]H,[13]C-edited-HSQC NMR spectrum of *E*-**10b**, *cis*/*trans* 6.7:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

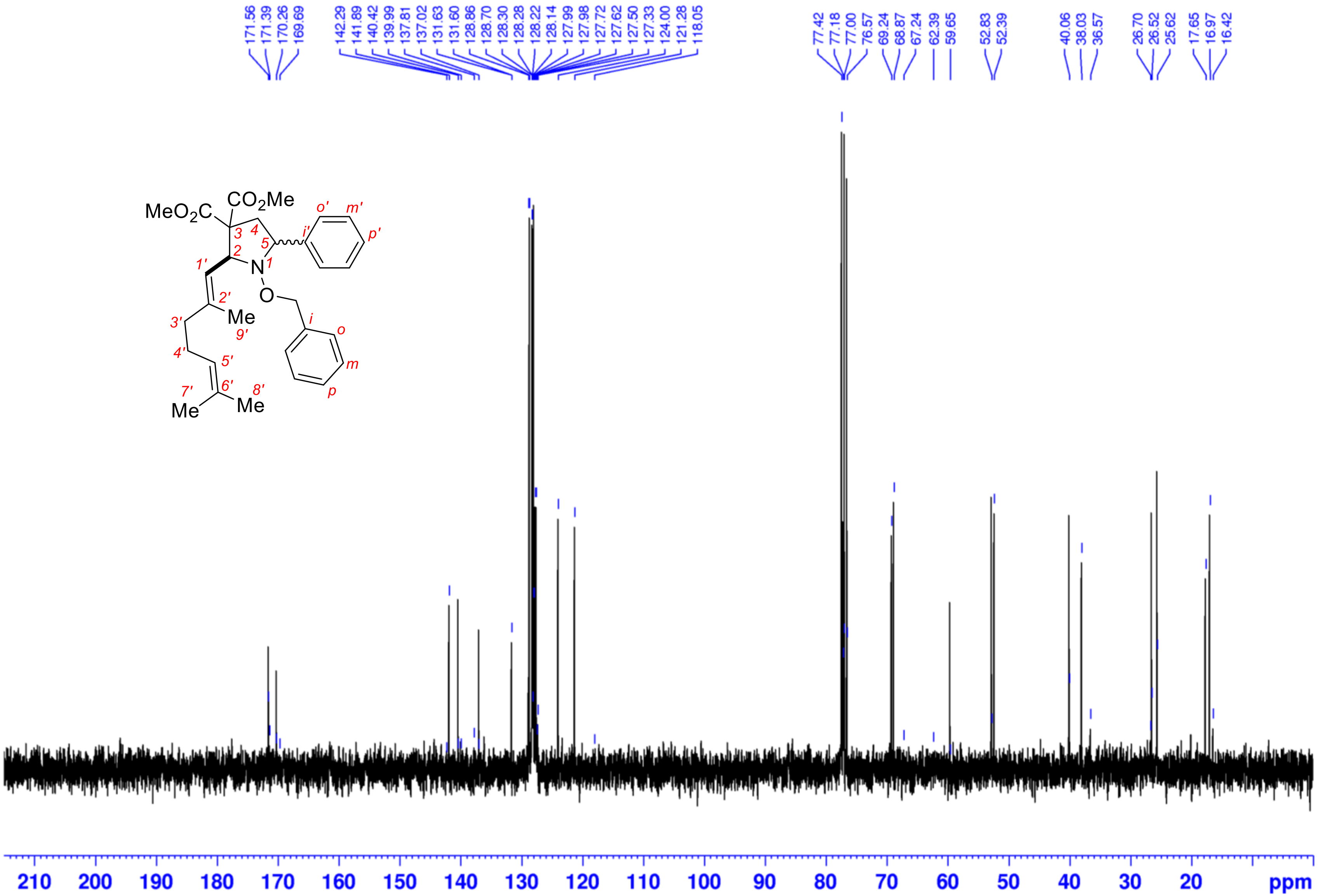


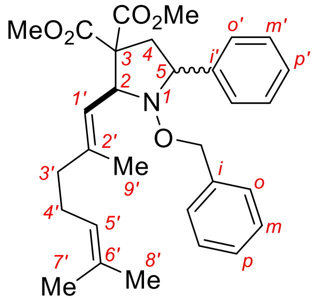

[1]H,[13]C-HMBC NMR spectrum of *E*-**10b**, *cis*/*trans* 6.7:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

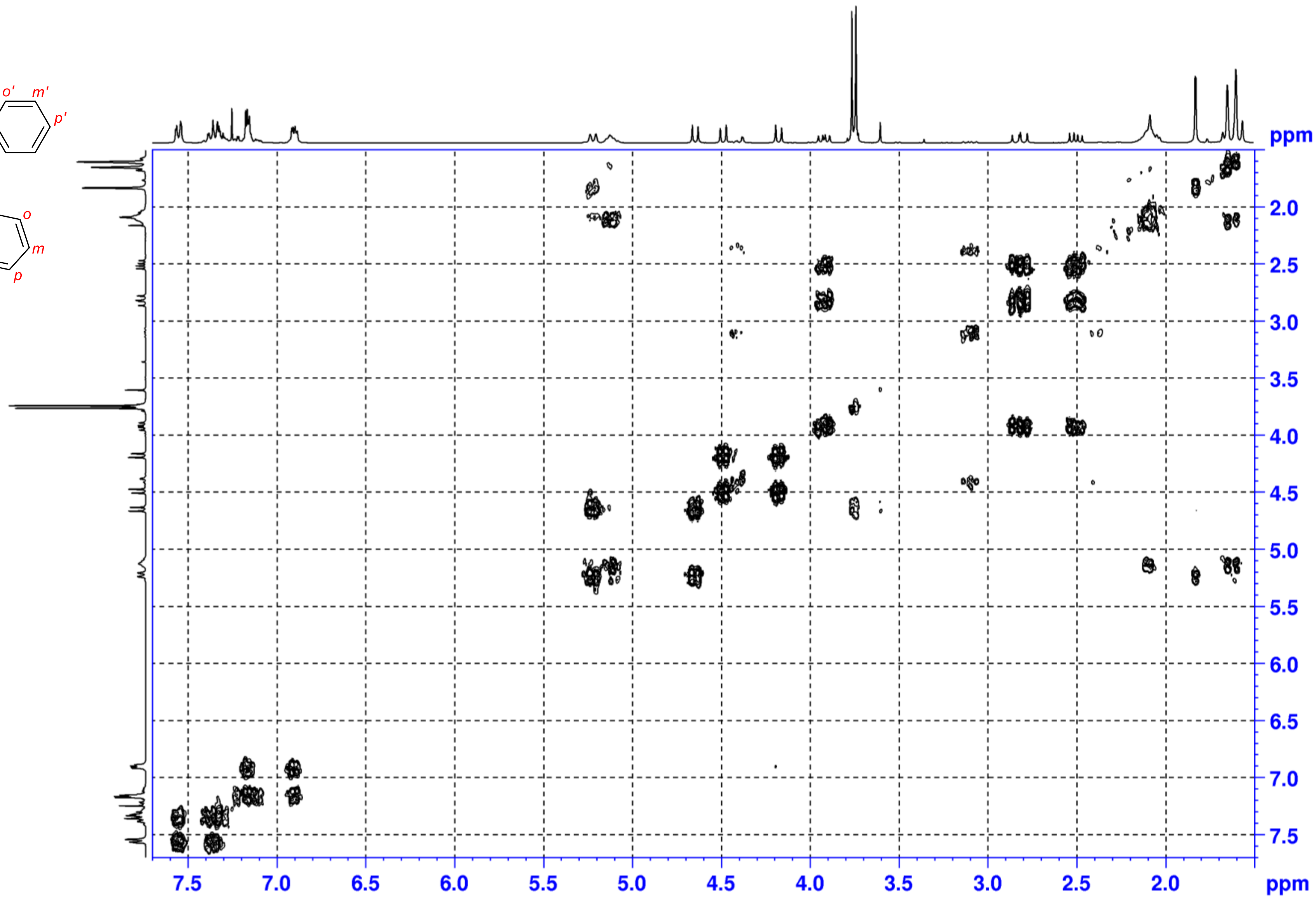



[1]H NMR spectrum of *E*-**10d**, *cis*/*trans* 6.4:1 (300.1 MHz, $CDCl_3$)

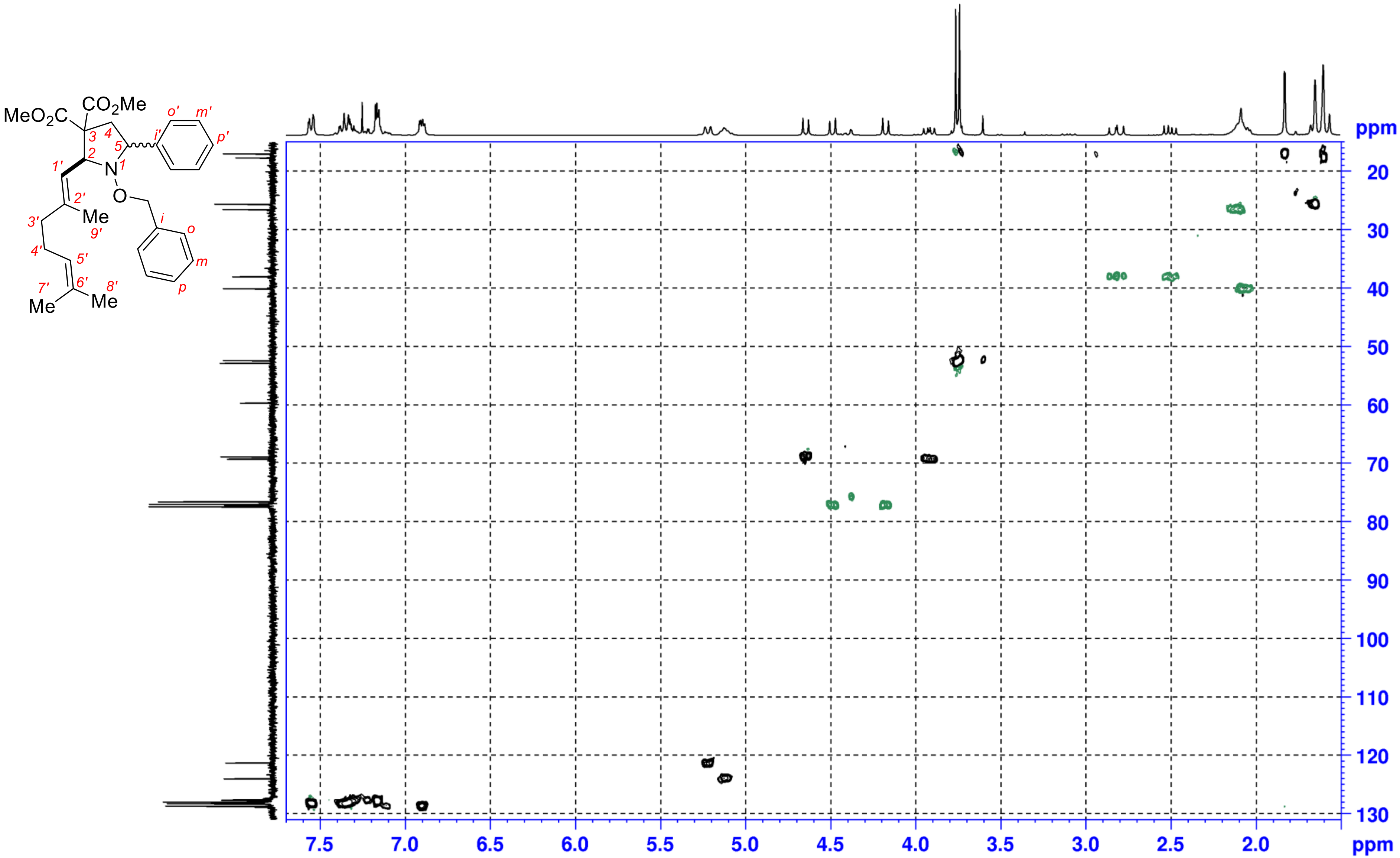



$^{13}$C NMR spectrum of *E*-**10d**, *cis*/*trans* 6.4:1 (75.5 MHz, $CDCl_3$)

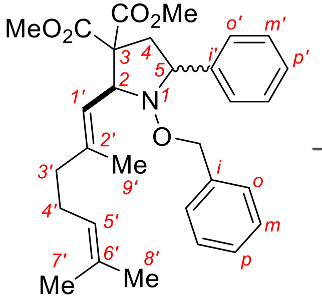


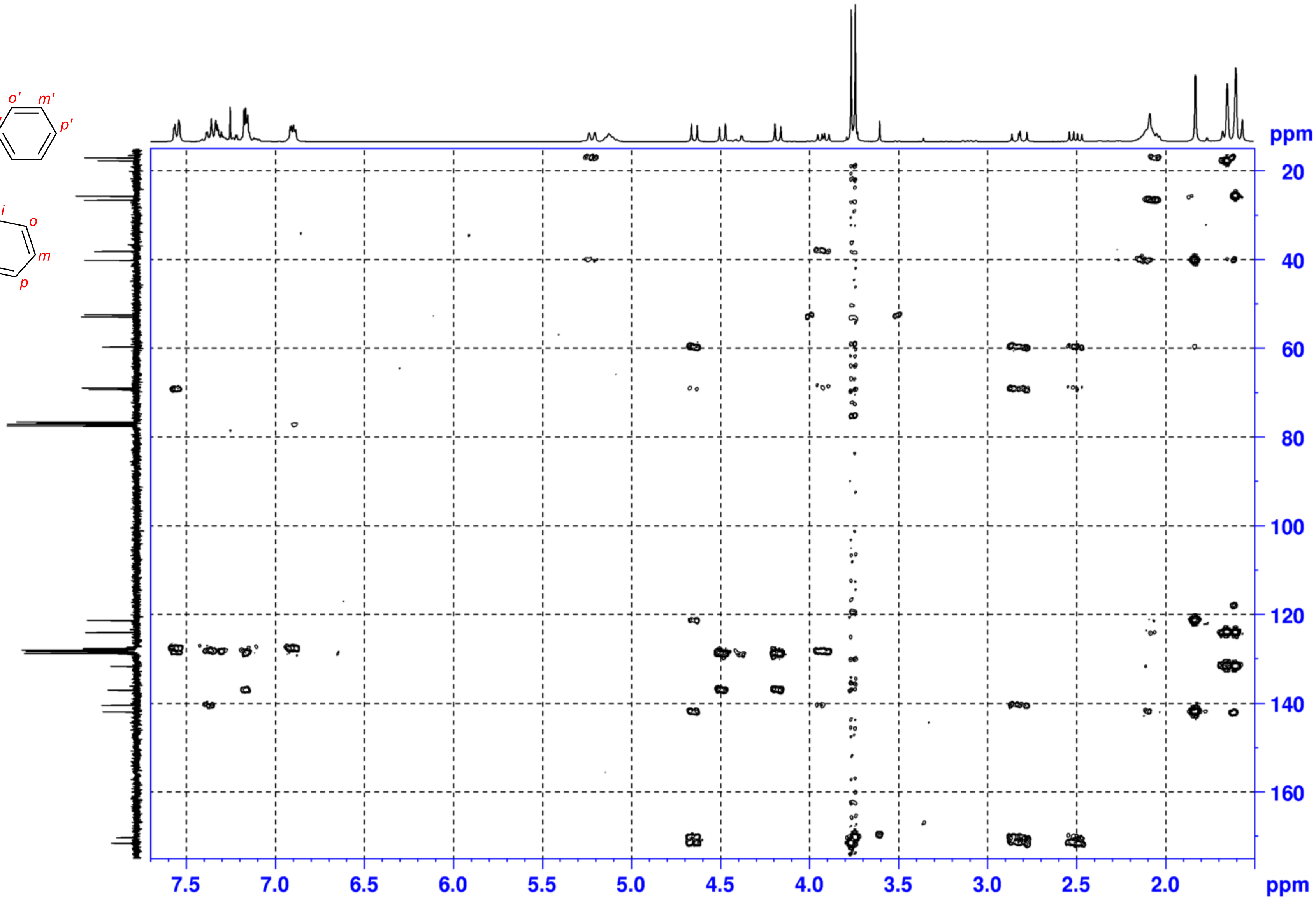




$^{1}$H,$^{1}$H-COSY NMR spectrum of *E*-**10d**, *cis*/*trans* 6.4:1 (300.1 MHz, $CDCl_3$)

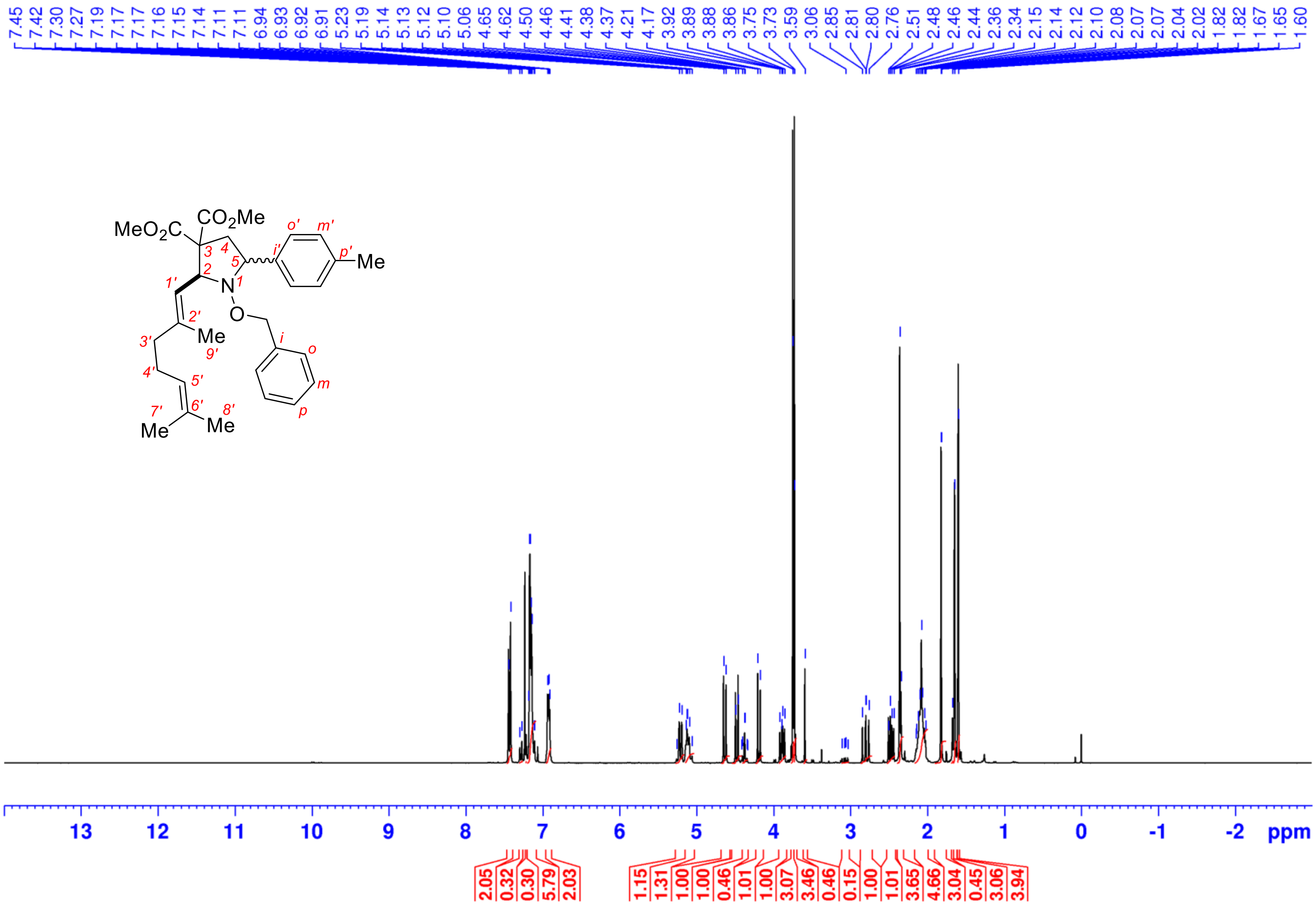



[1]H,[13]C-edited-HSQC NMR spectrum of *E*-**10d**, *cis*/*trans* 6.4:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

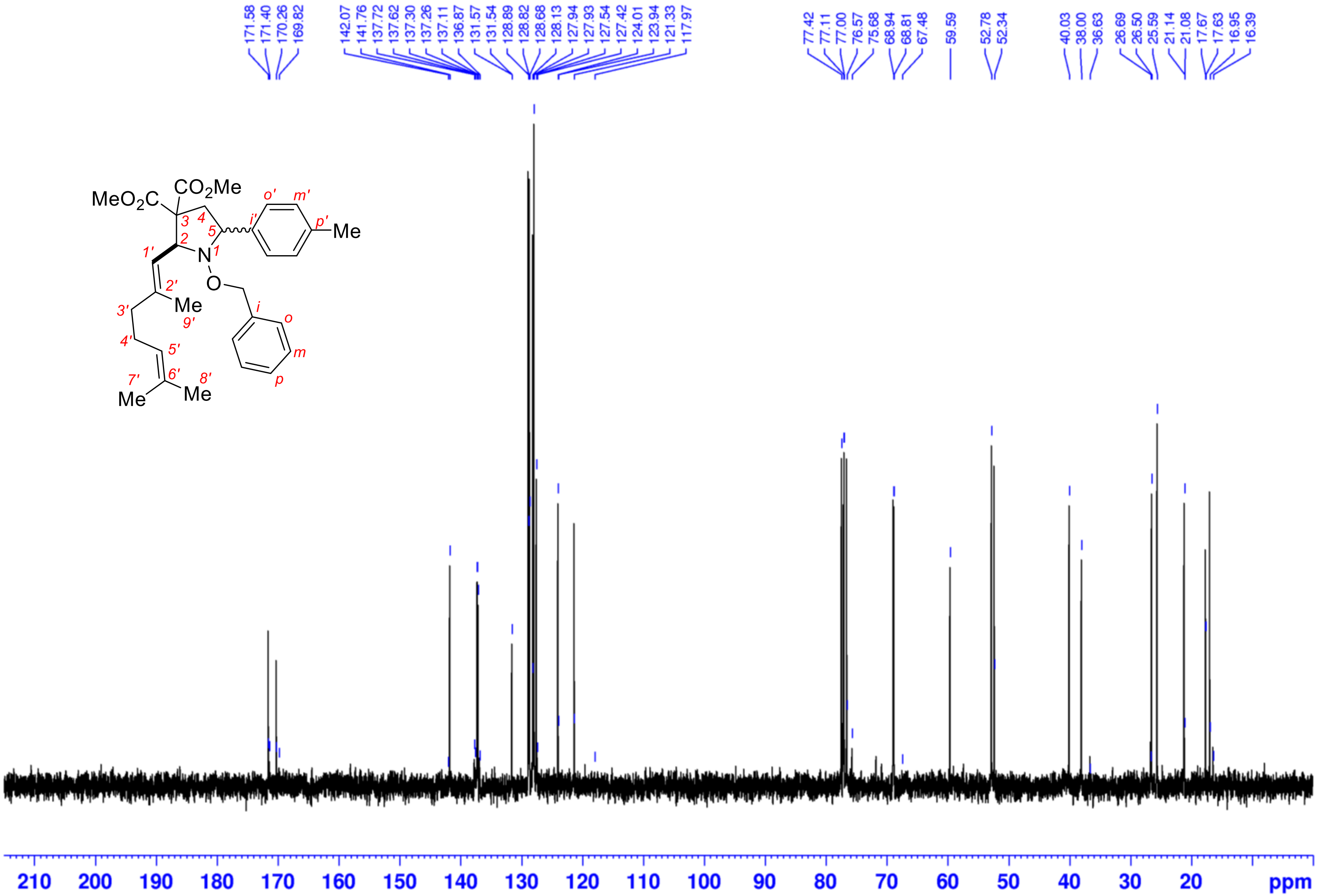


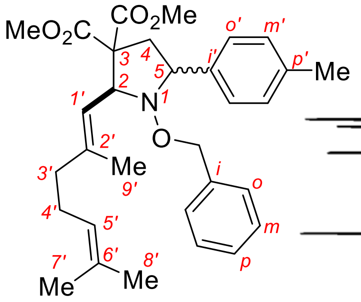

$^{1}H,^{13}C$-HMBC NMR spectrum of *E*-**10d**, *cis*/*trans* 6.4:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

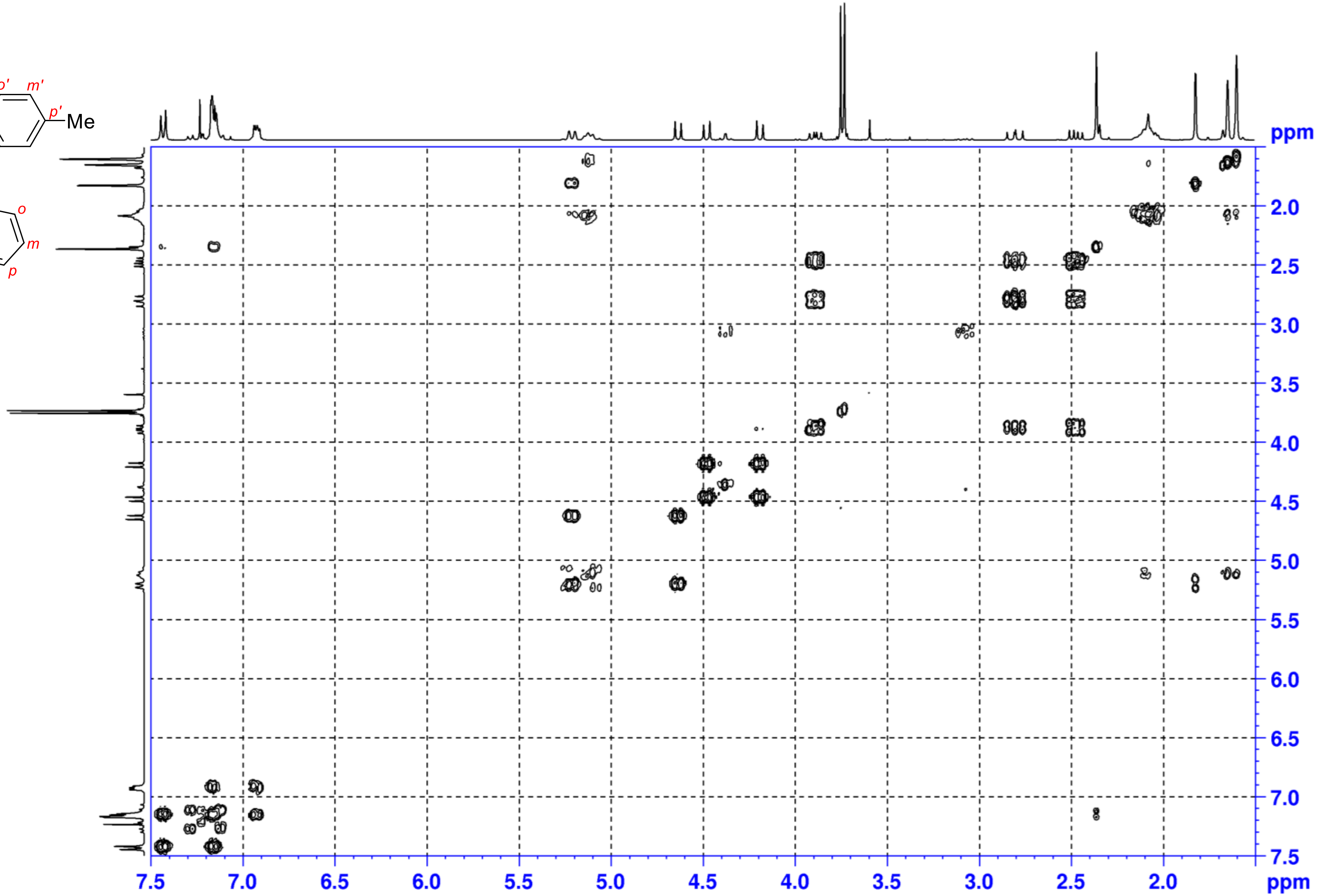


[1]H NMR spectrum of *E*-**10f**, *cis*/*trans* 6.7:1 (300.1 MHz, $CDCl_3$)

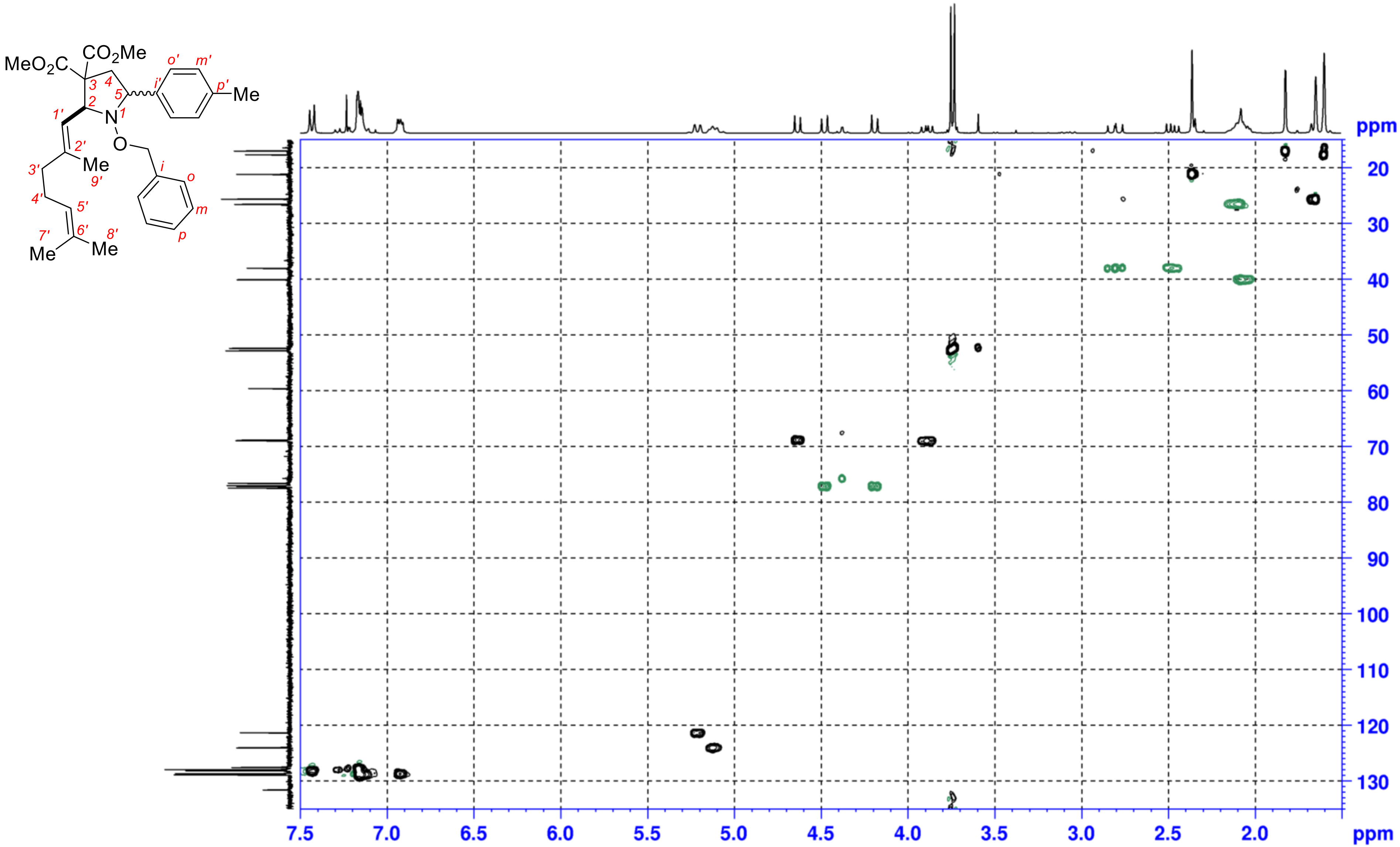



$^{13}$C NMR spectrum of *E*-**10f**, *cis*/*trans* 6.7:1 (75.5 MHz, CDCl$_3$)

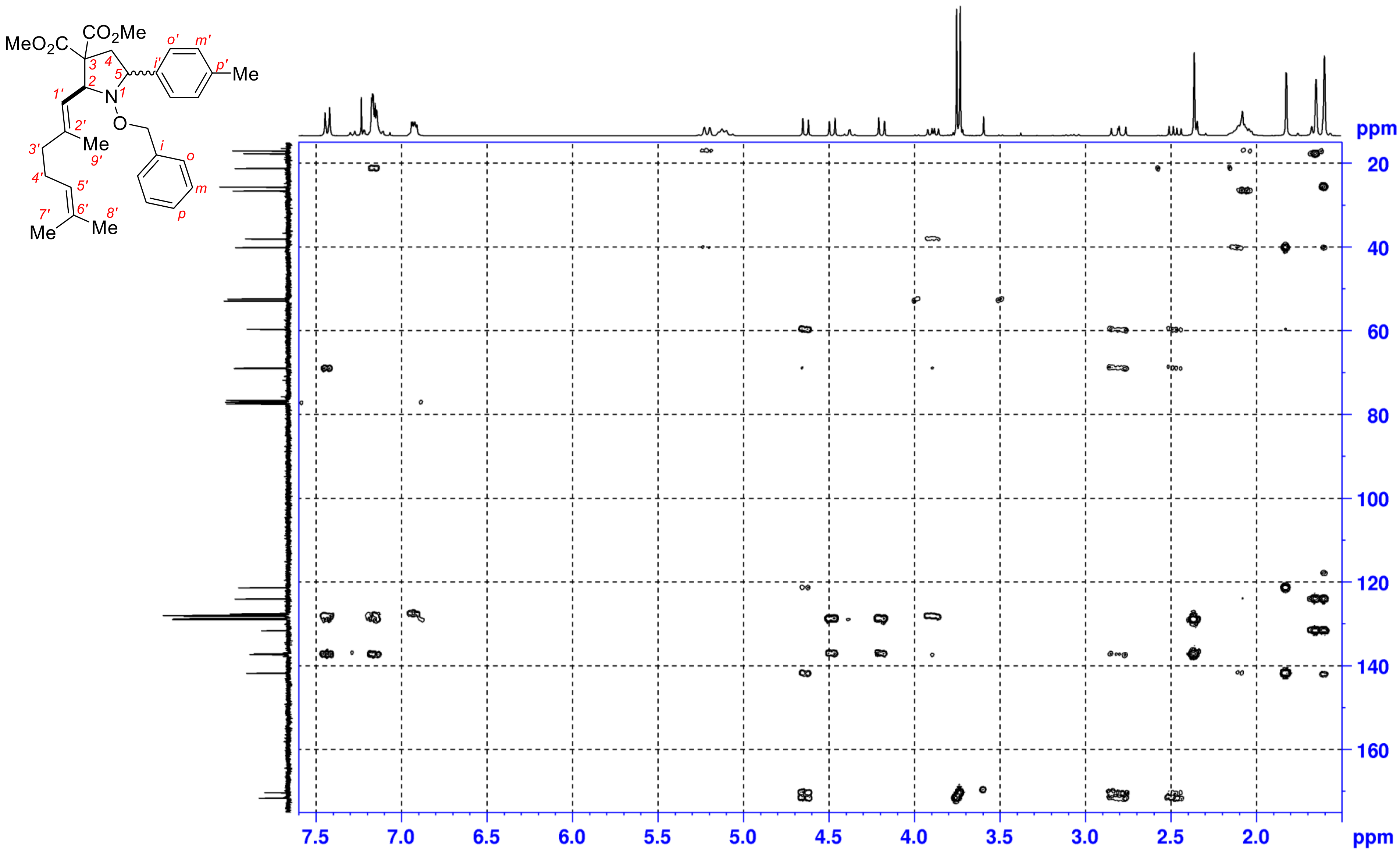




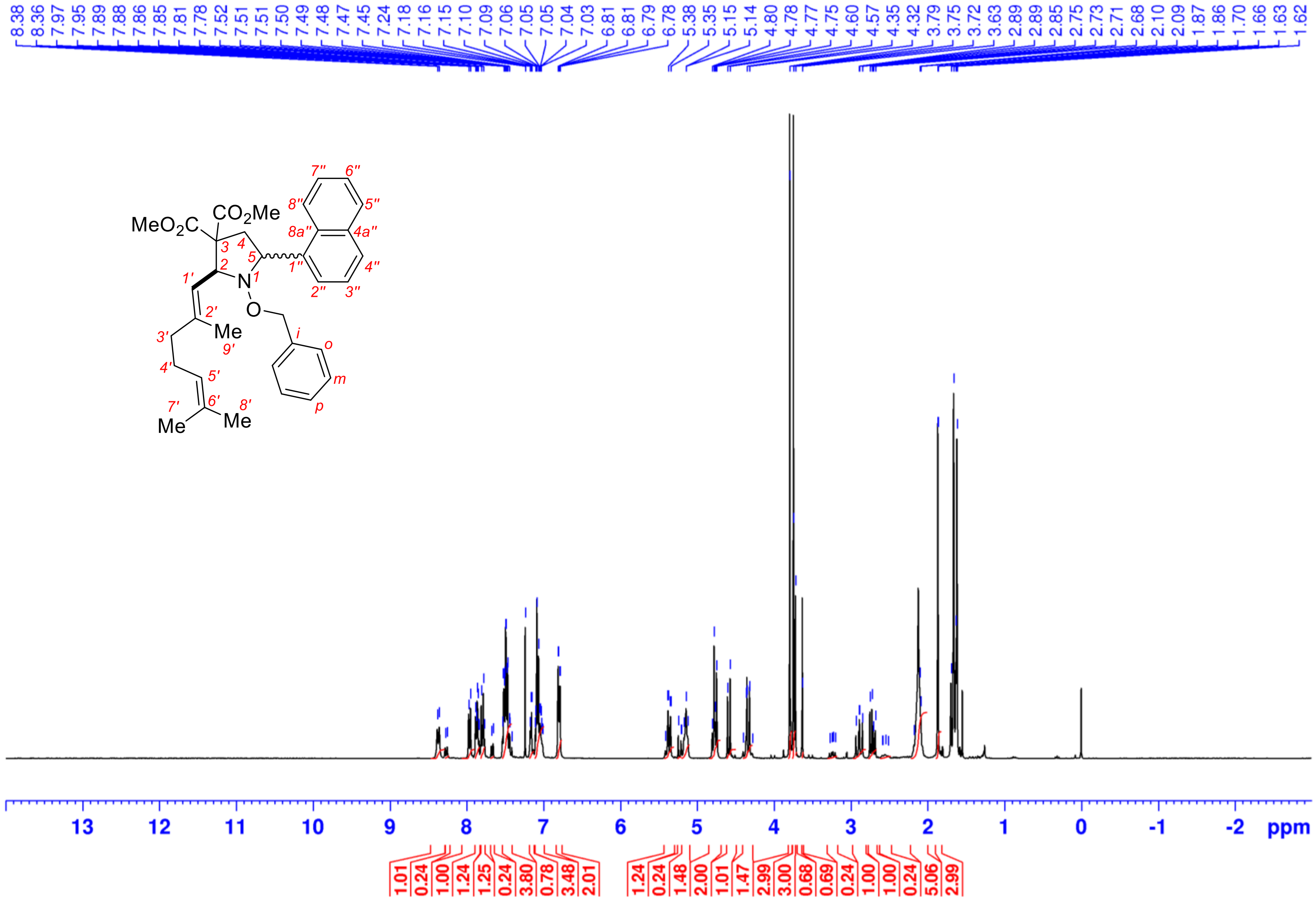
$^{1}H,^{1}H$-COSY NMR spectrum of *E*-**10f**, *cis*/*trans* 6.7:1 (300.1 MHz, $CDCl_3$)



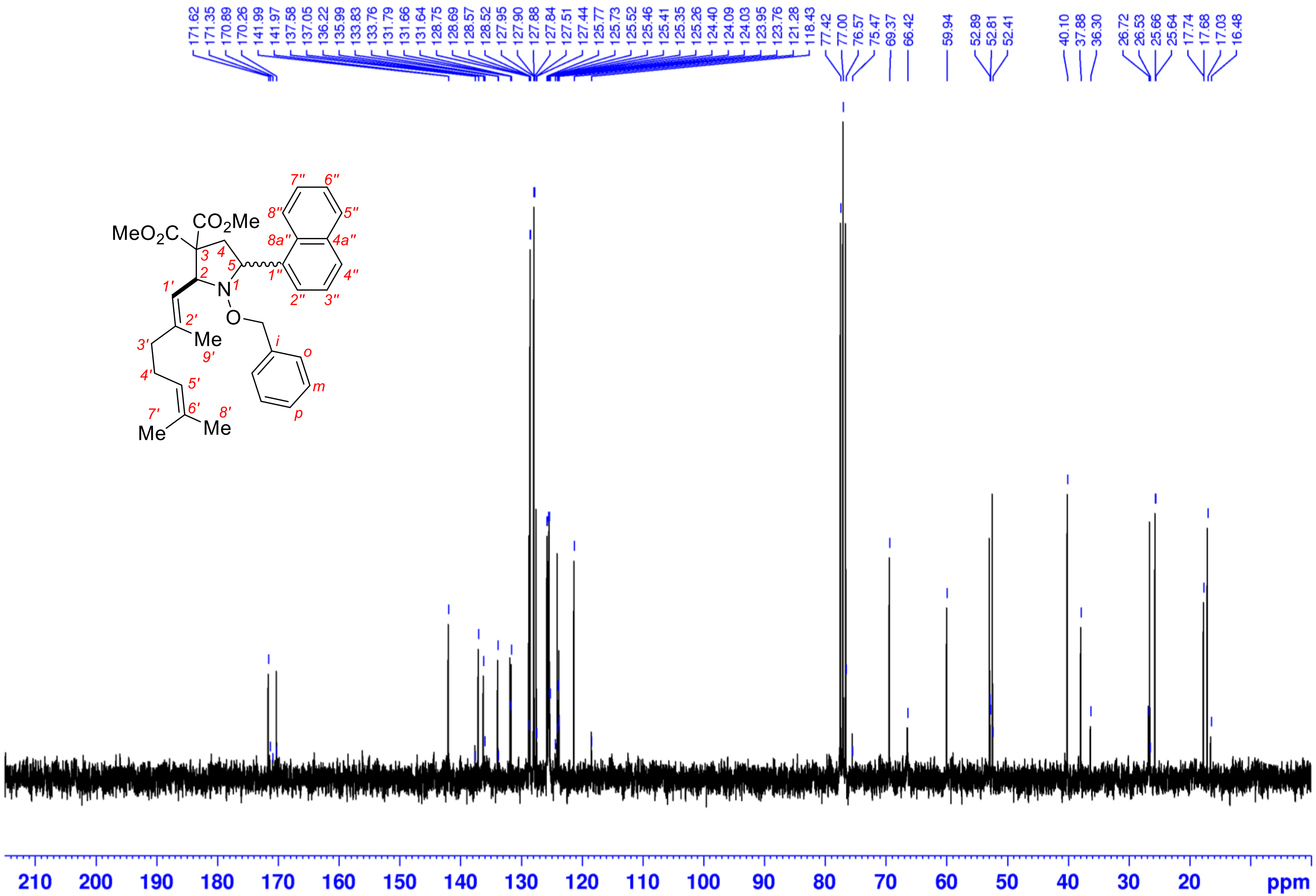

$^{1}$H,$^{13}$C-edited-HSQC NMR spectrum of *E*-**10f**, *cis*/*trans* 6.7:1 ($^{1}$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)



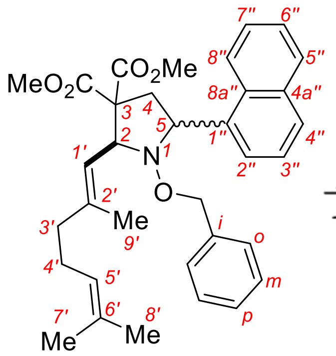

[1]H,[13]C-HMBC NMR spectrum of *E*-**10f**, *cis*/*trans* 6.7:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

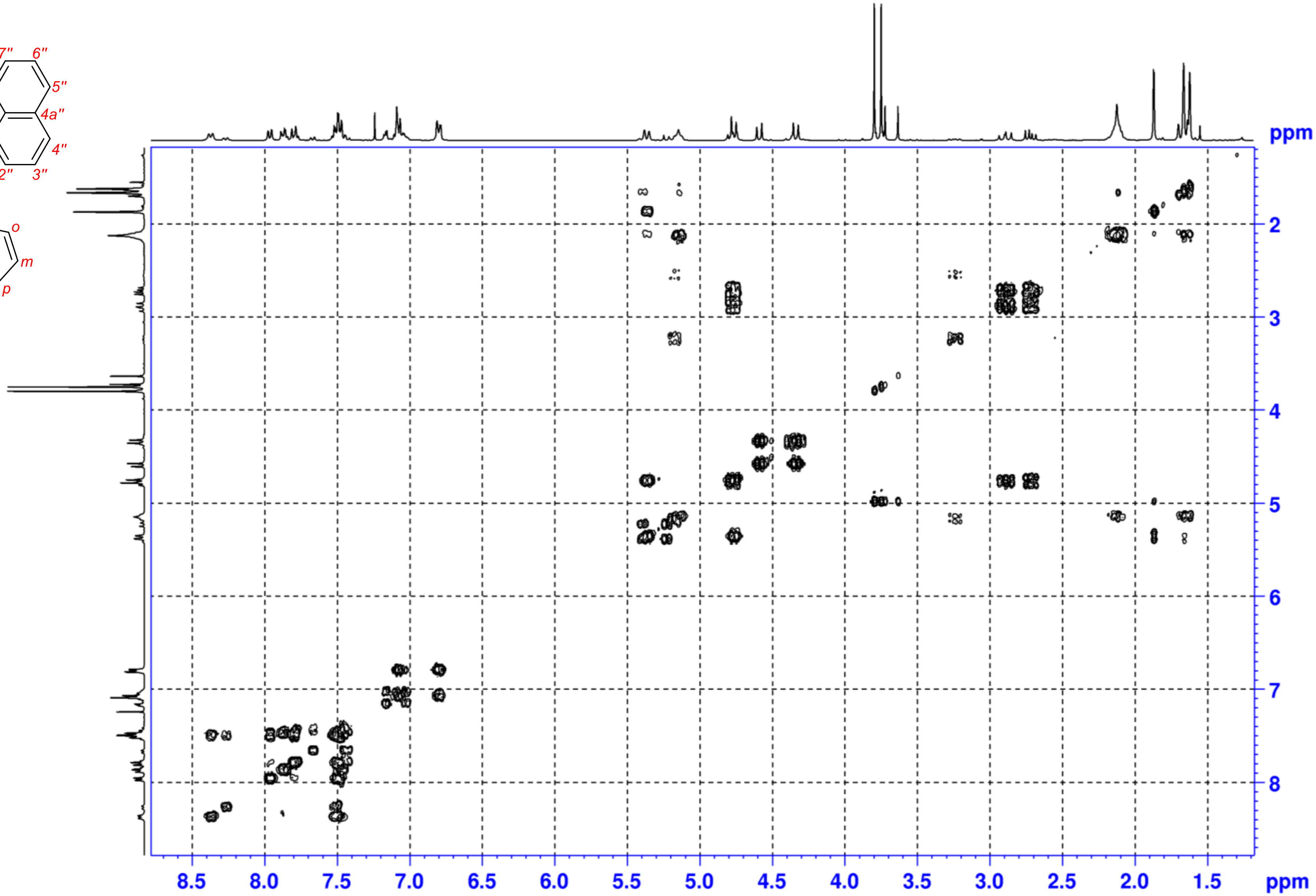


[1]H NMR spectrum of *E*-**10g**, *cis*/*trans* 4.2:1 (300.1 MHz, $CDCl_3$)

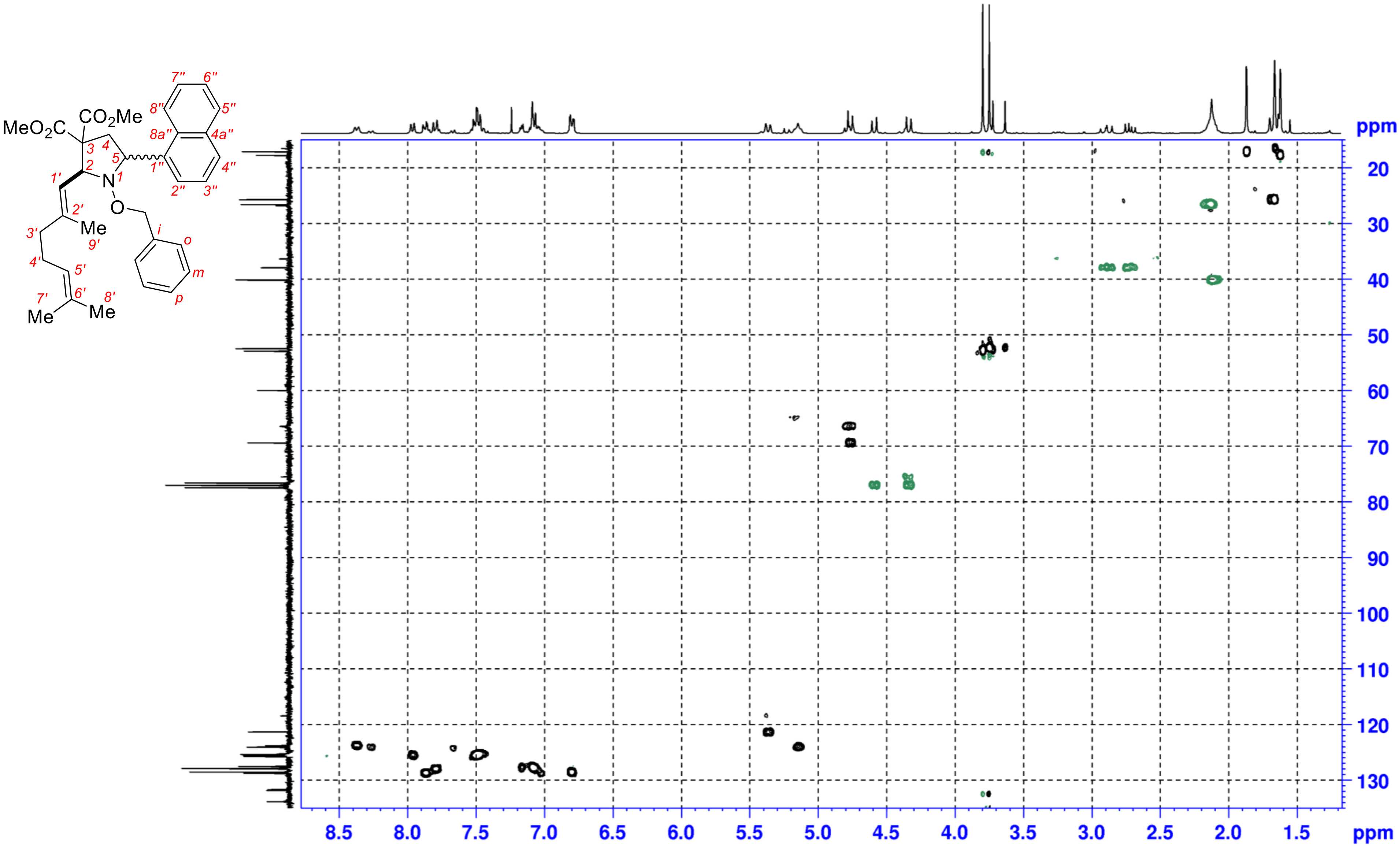


$^{13}$C NMR spectrum of *E*-**10g**, *cis*/*trans* 4.2:1 (75.5 MHz, $CDCl_3$)

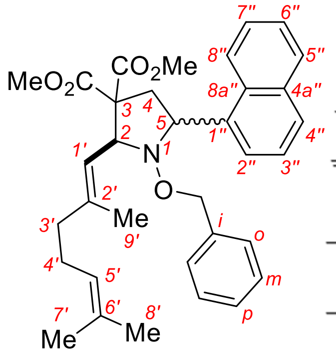


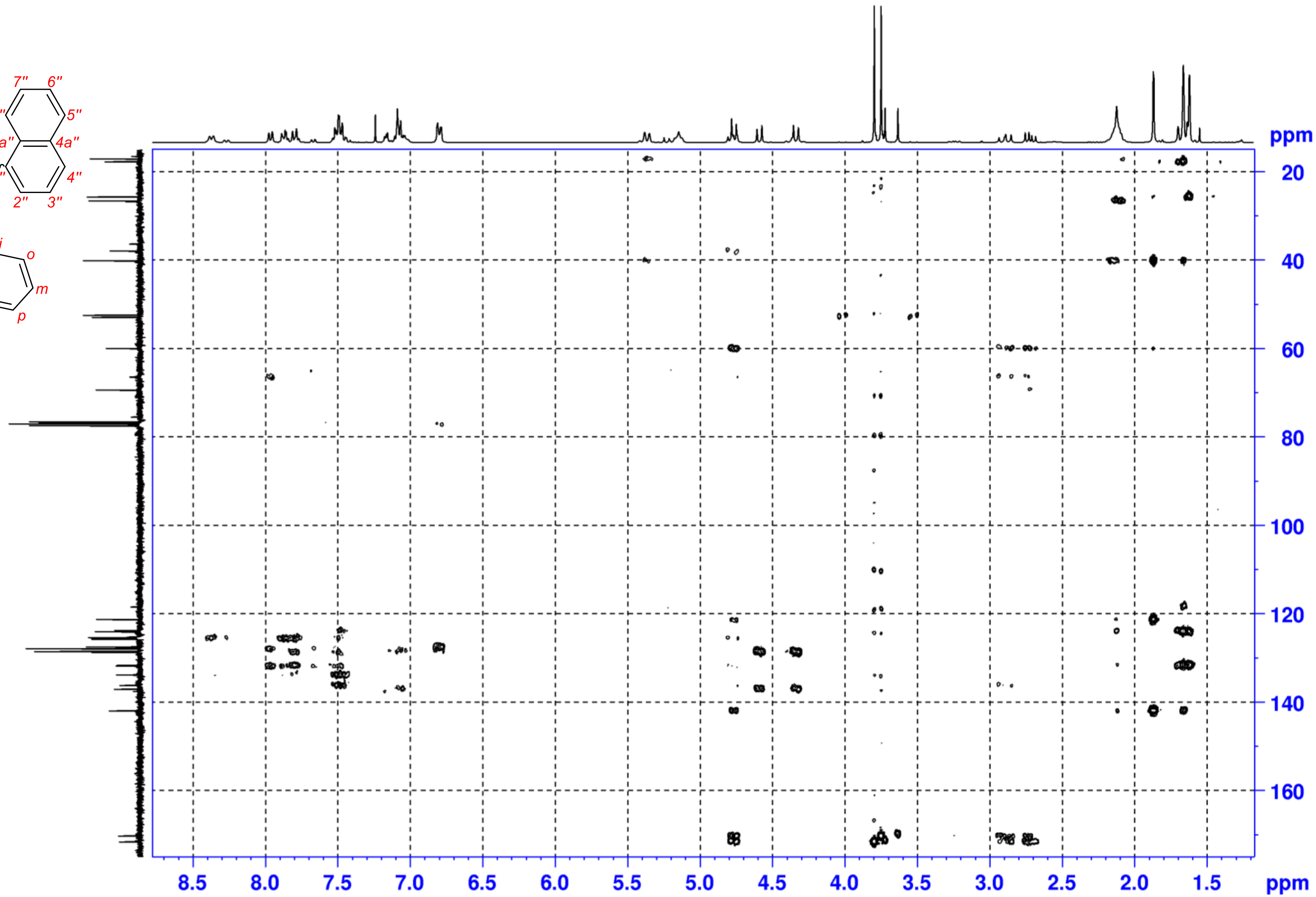




[1]H,[1]H-COSY NMR spectrum of *E*-**10g**, *cis*/*trans* 4.2:1 (300.1 MHz, $CDCl_3$)

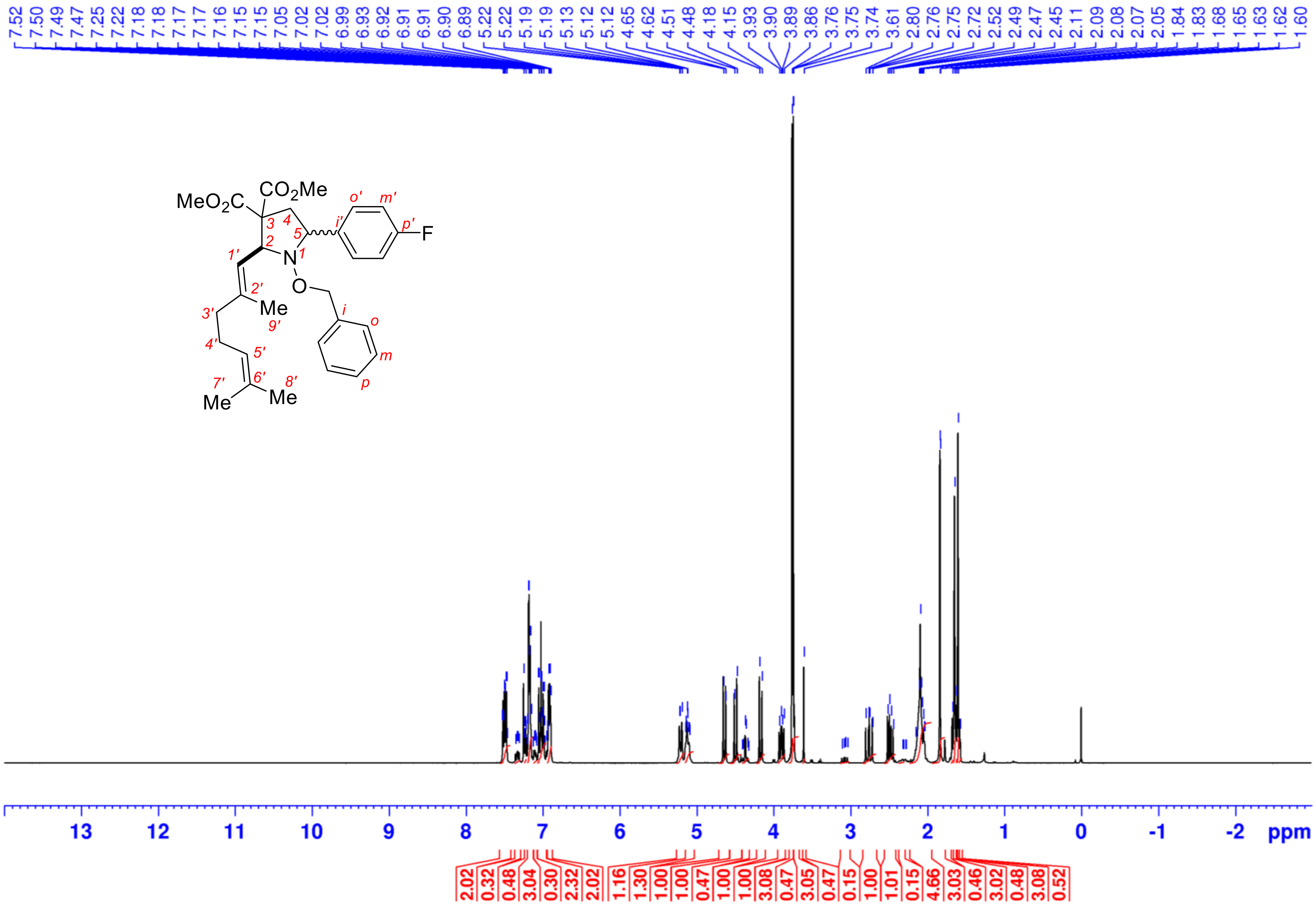



$^{1}$H,$^{13}$C-edited-HSQC NMR spectrum of *E*-**10g**, *cis*/*trans* 4.2:1 ($^{1}$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)

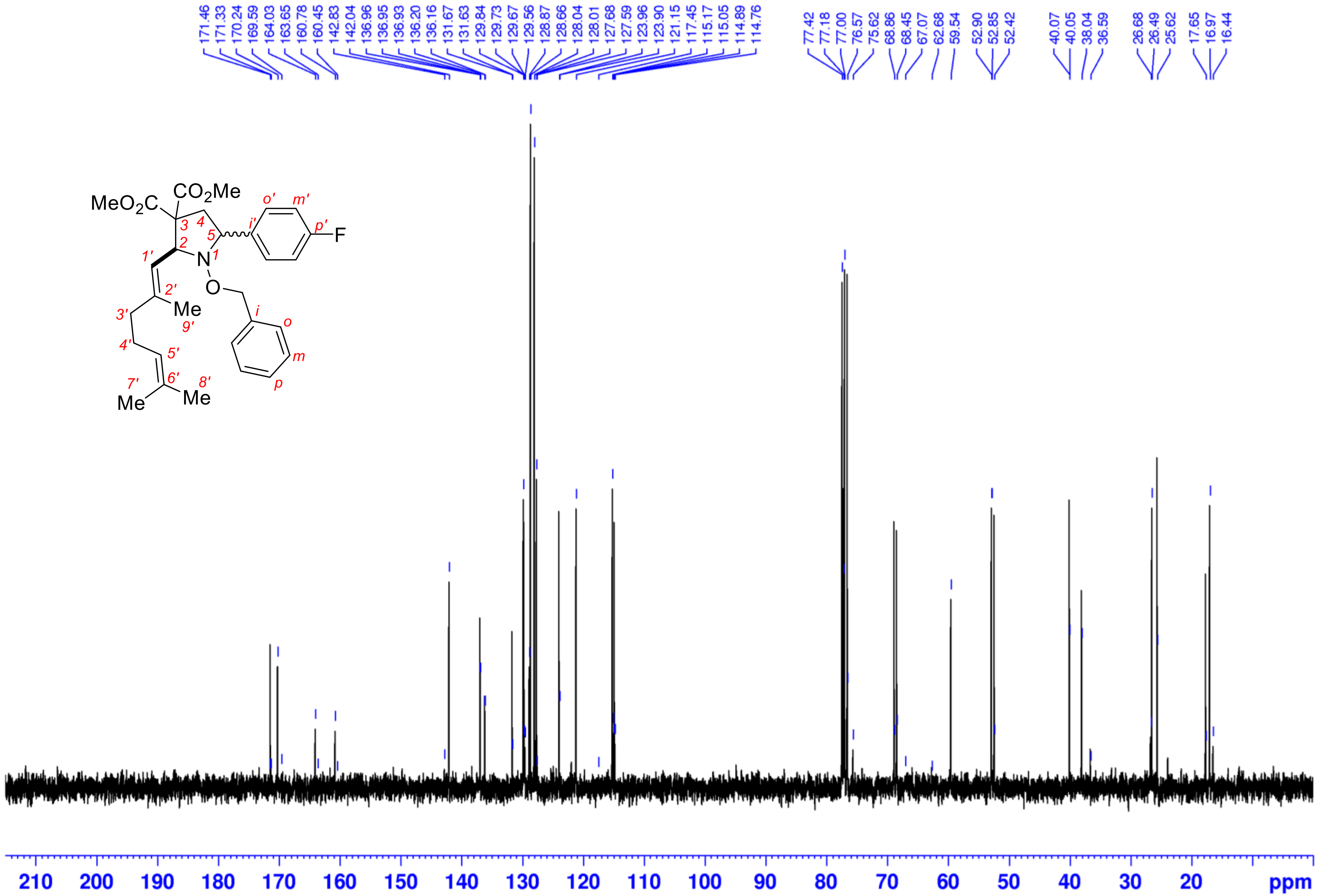


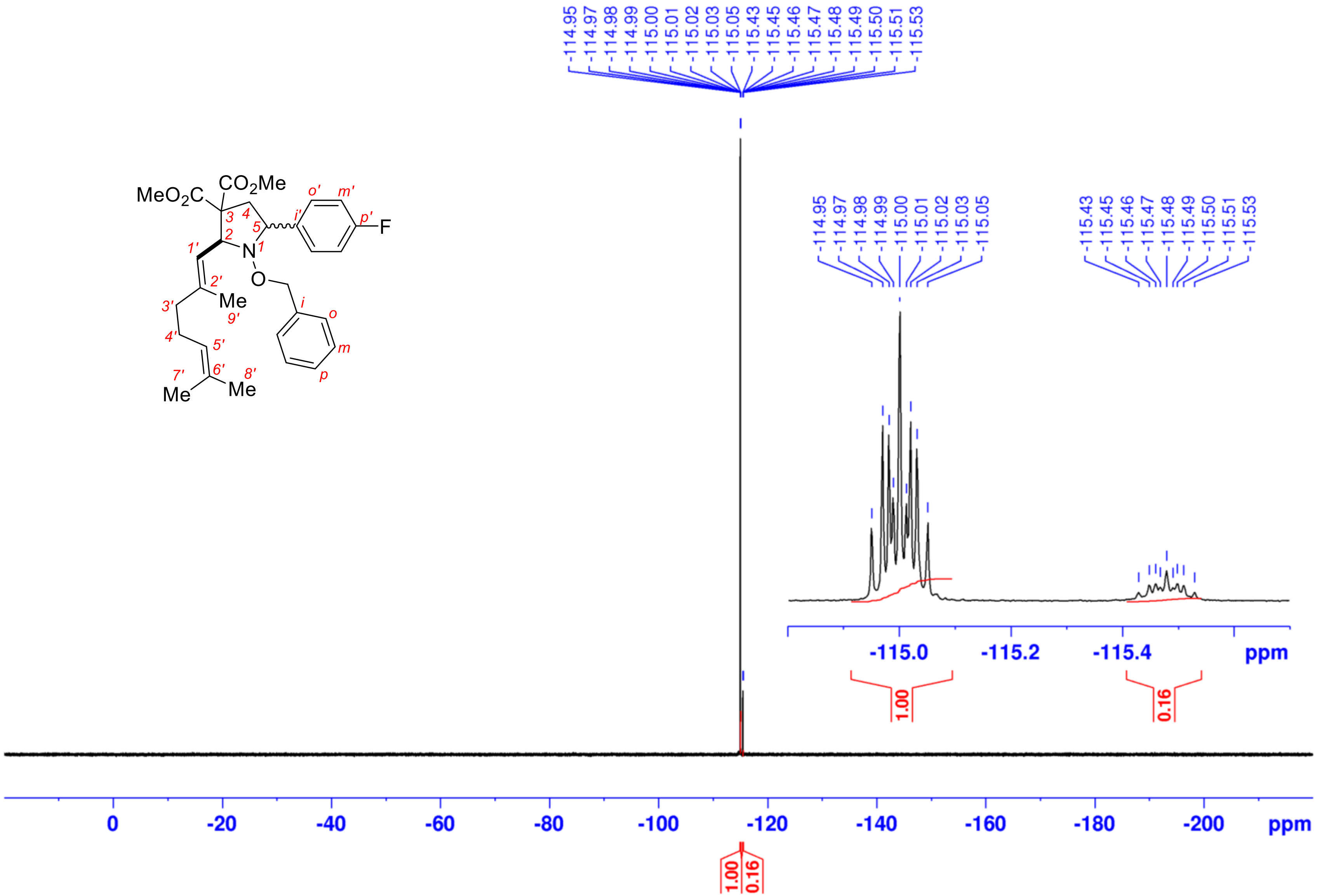

$^{1}H,^{13}C$-HMBC NMR spectrum of *E*-**10g**, *cis*/*trans* 4.2:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)



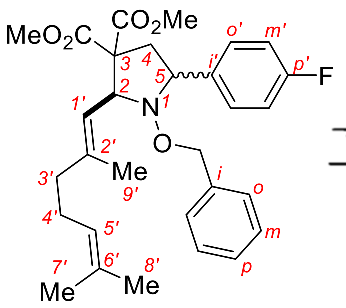

[1]H NMR spectrum of *E*-**10h**, *cis*/*trans* 6.7:1 (300.1 MHz, $CDCl_3$)

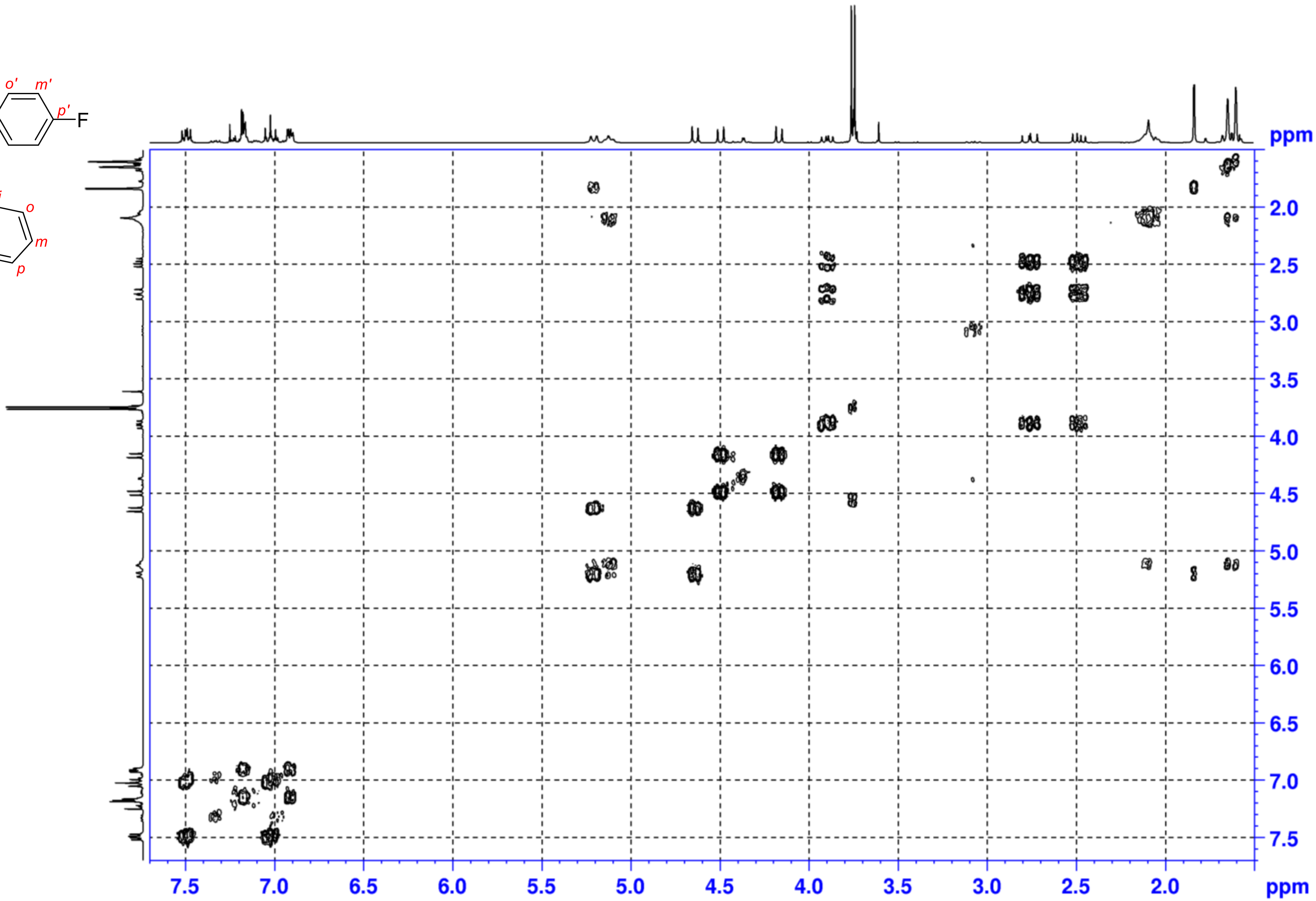



$^{13}$C NMR spectrum of *E*-**10h**, *cis*/*trans* 6.7:1 (75.5 MHz, $CDCl_3$)

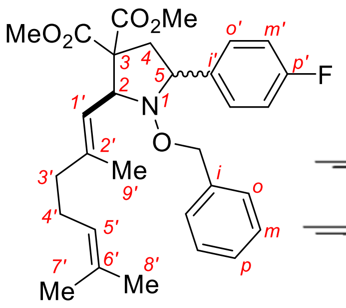


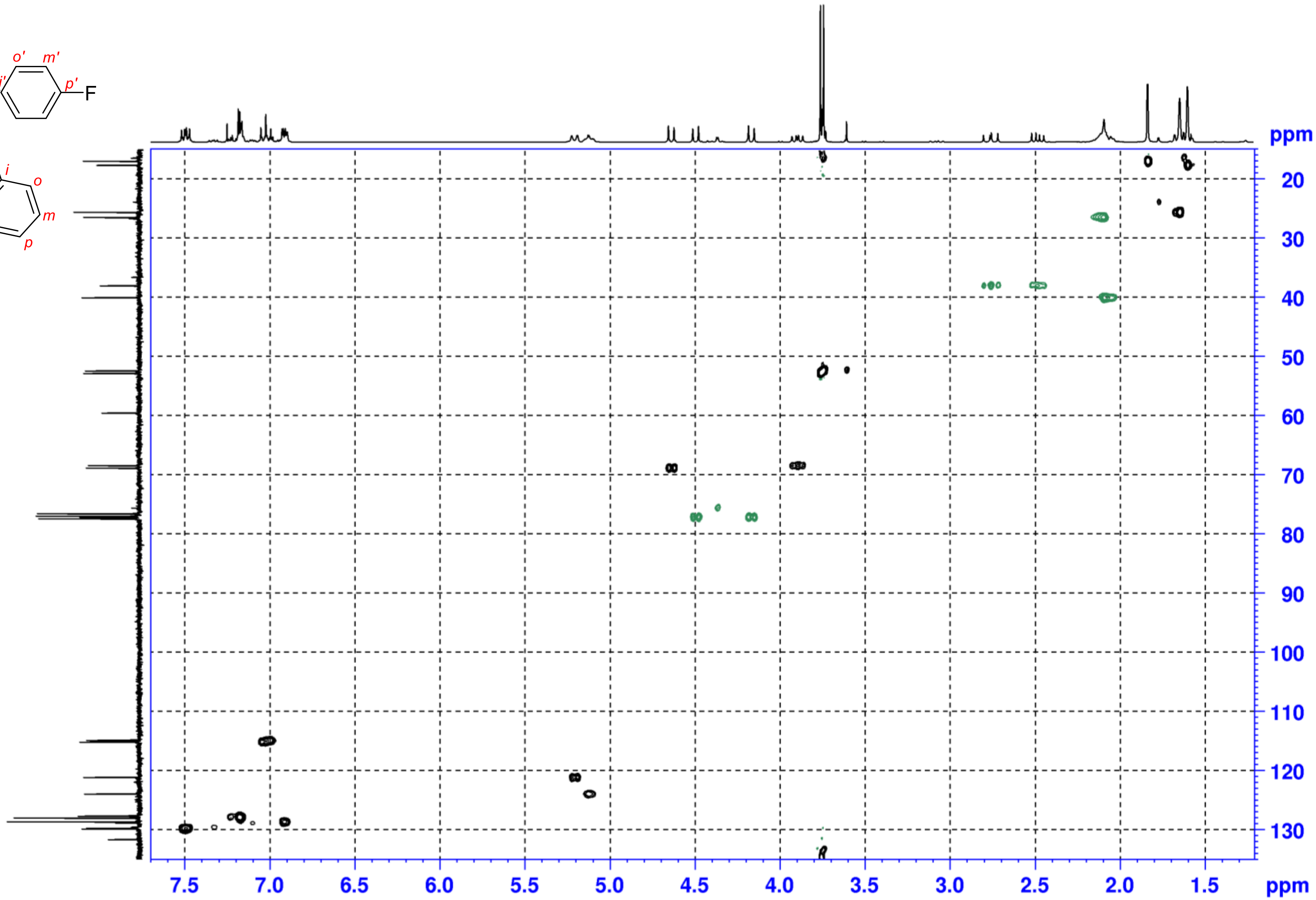
$^{19}$F NMR spectrum of *E*-**10h**, *cis*/*trans* 6.7:1 (282.5 MHz, $CDCl_3$)



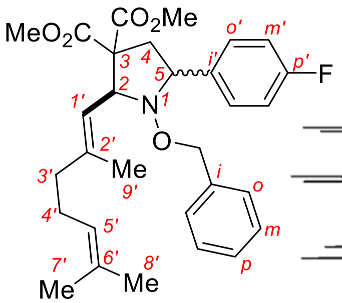



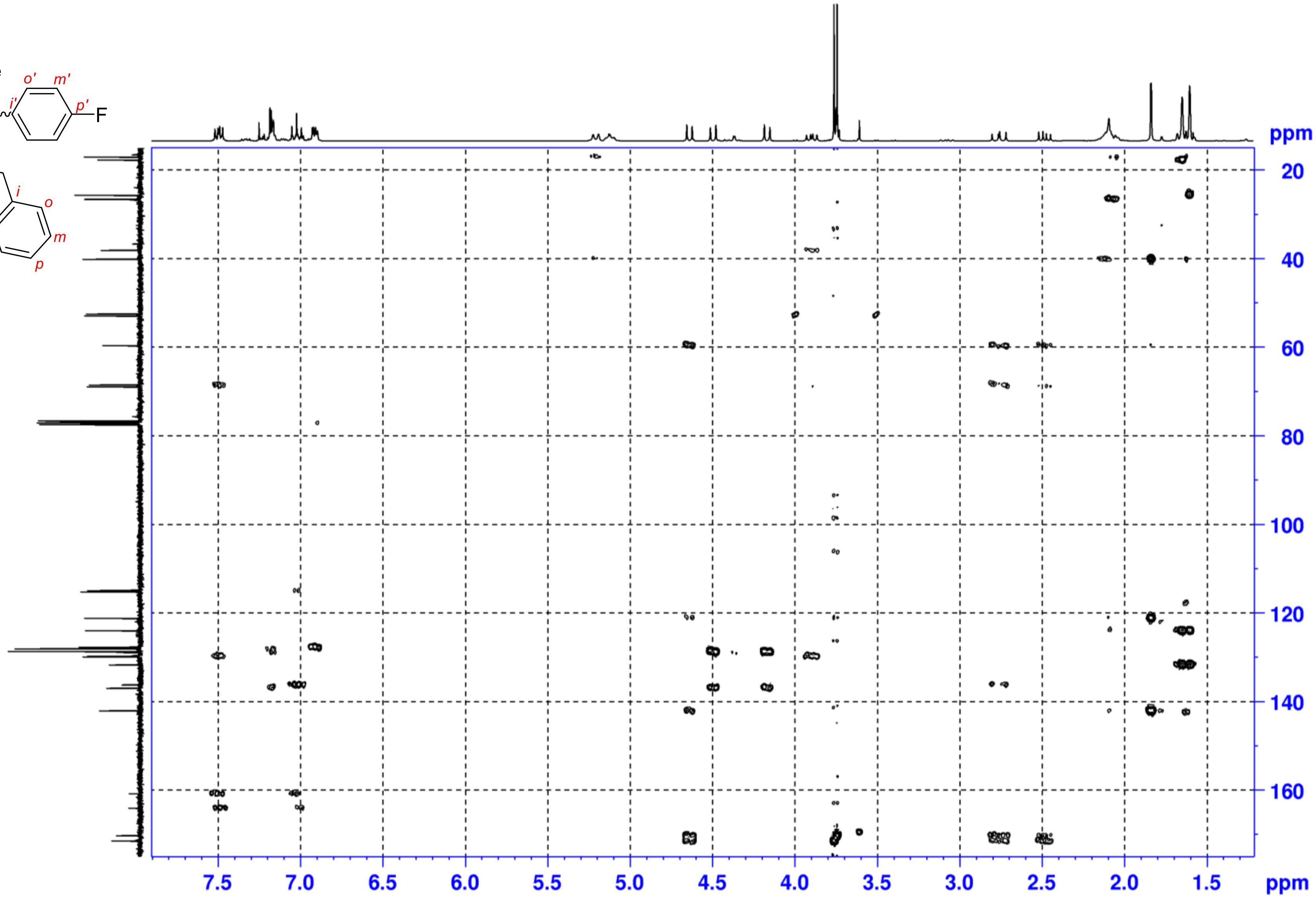

$^{1}H,^{1}H$-COSY NMR spectrum of *E*-**10h**, *cis*/*trans* 6.7:1 (300.1 MHz, $CDCl_3$)



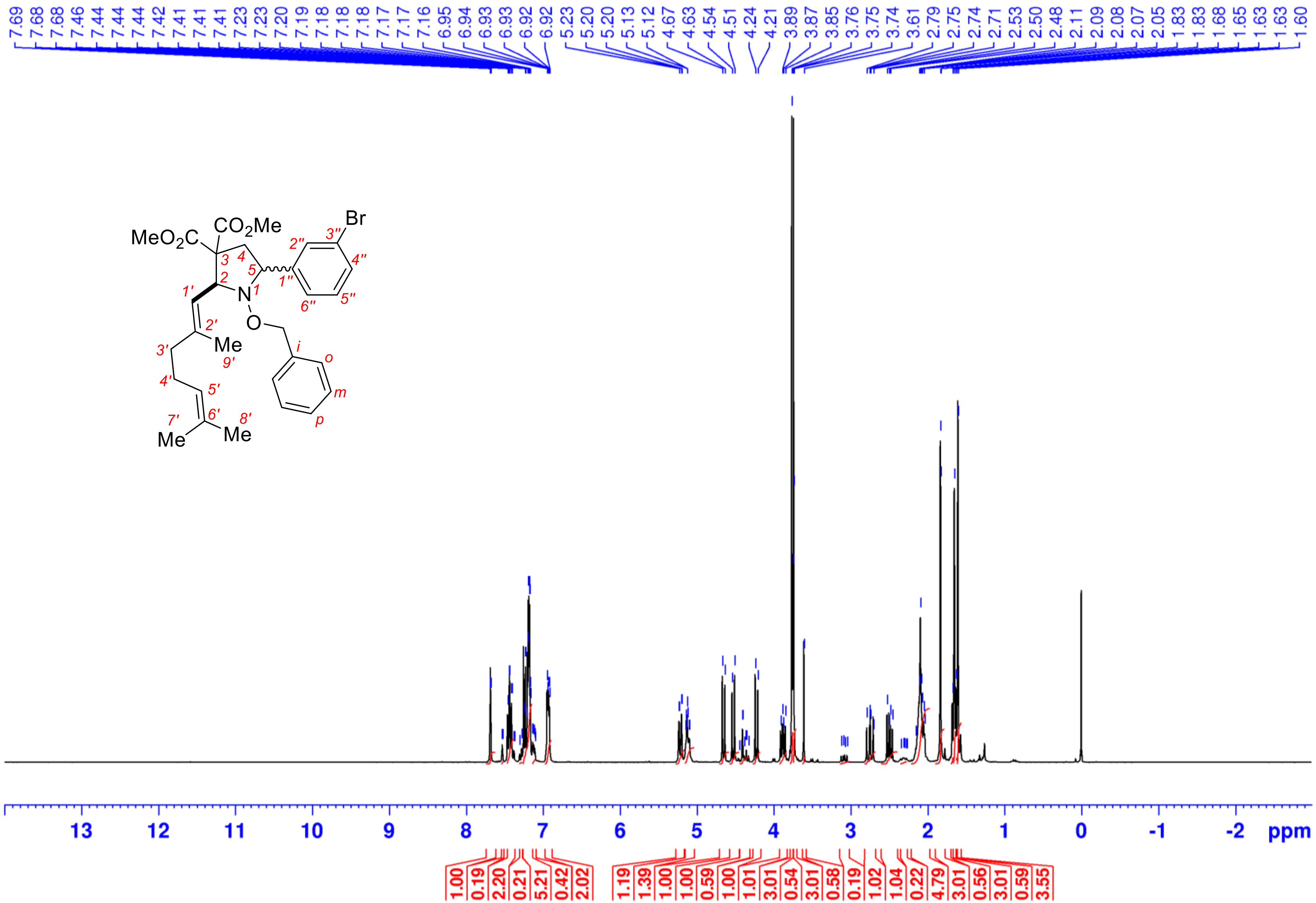




$^{1}$H,$^{13}$C-edited-HSQC NMR spectrum of *E*-**10h**, *cis*/*trans* 6.7:1 ($^{1}$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)

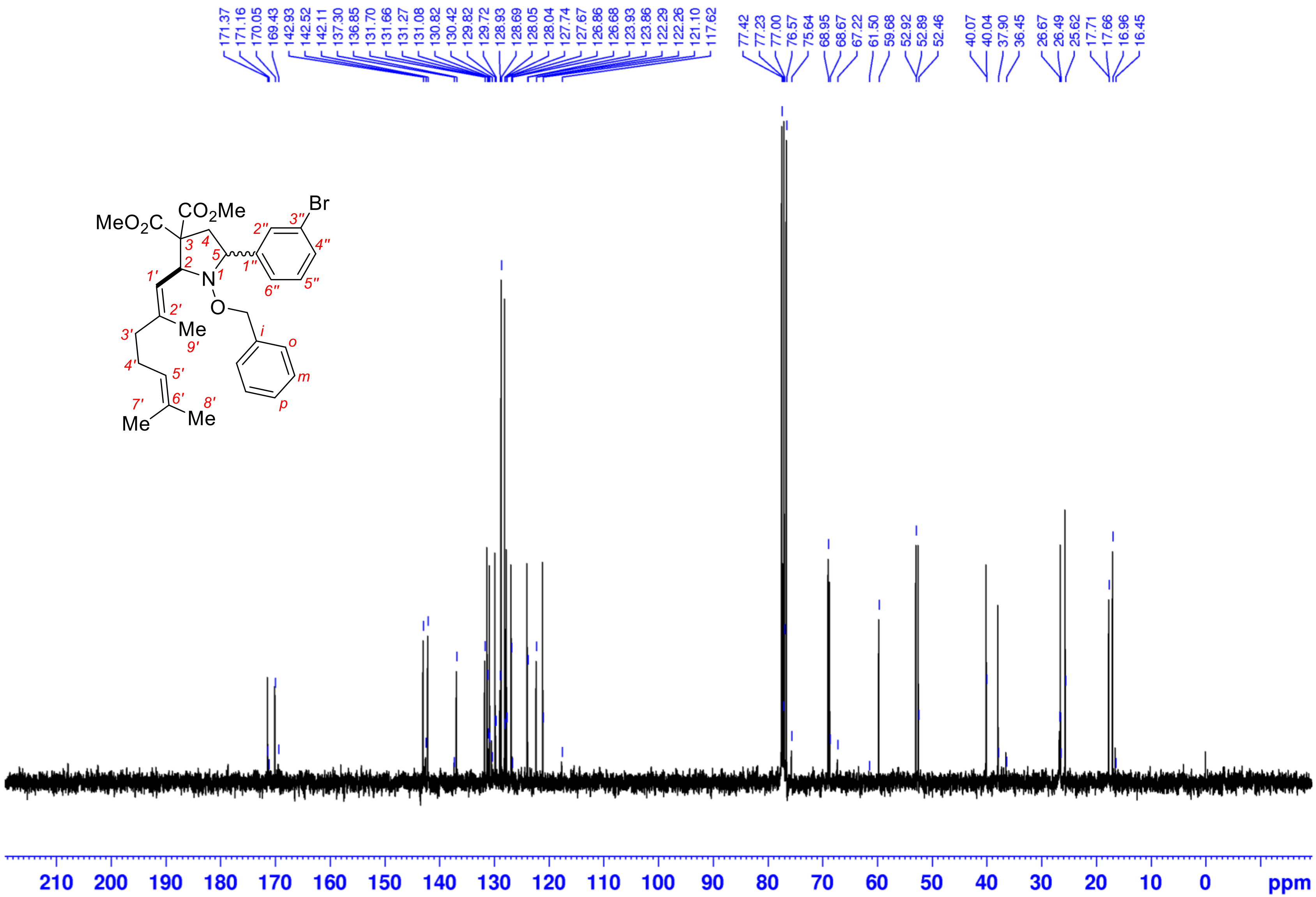




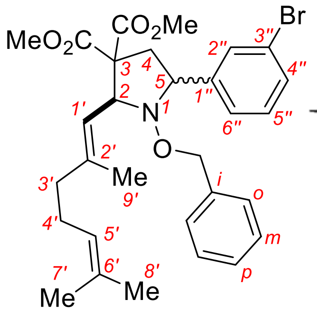
$^{1}H,^{13}C$-HMBC NMR spectrum of *E*-**10h**, *cis*/*trans* 6.7:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

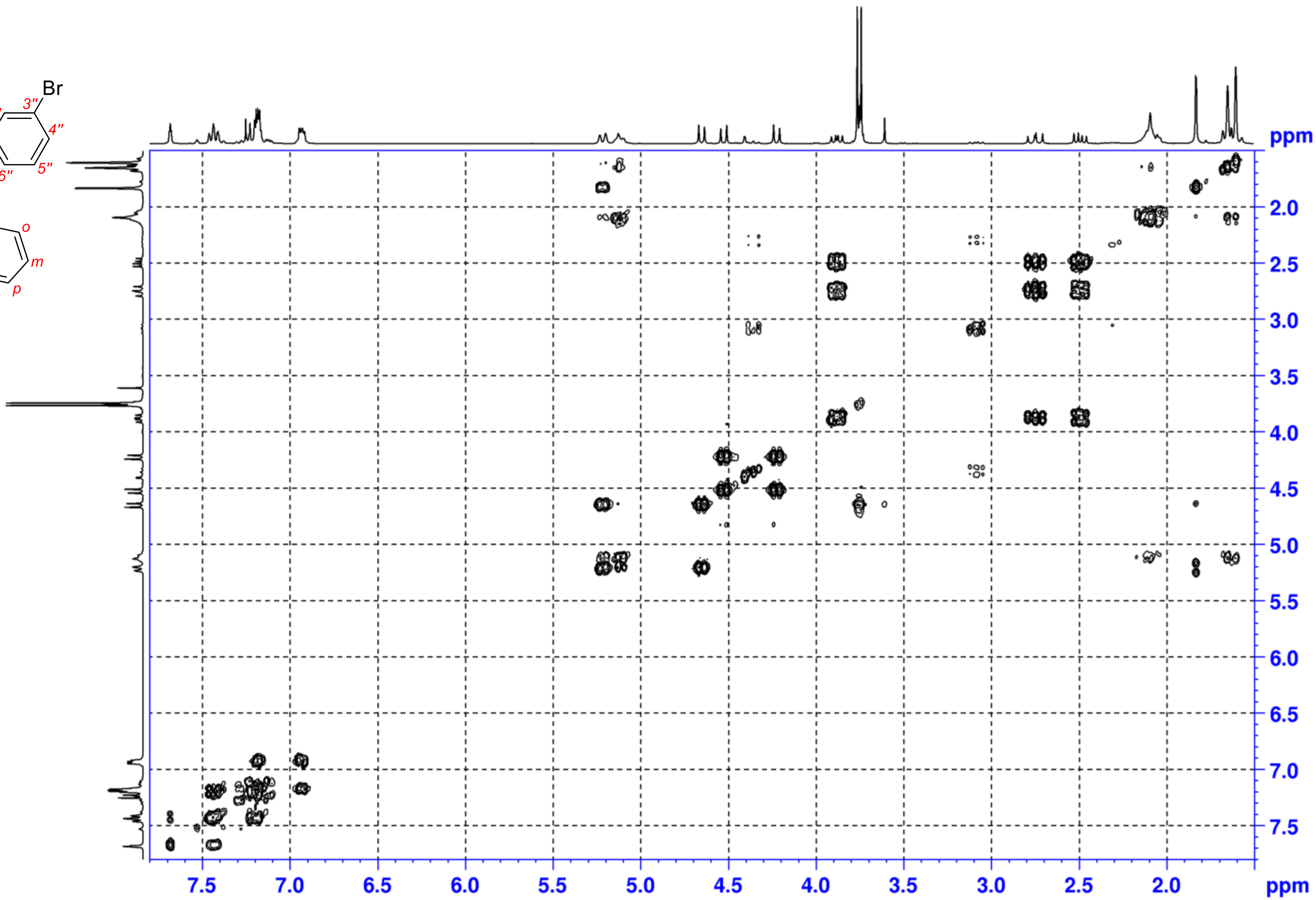


[1]H NMR spectrum of *E*-**10i**, *cis*/*trans* 5.3:1 (300.1 MHz, $CDCl_3$)

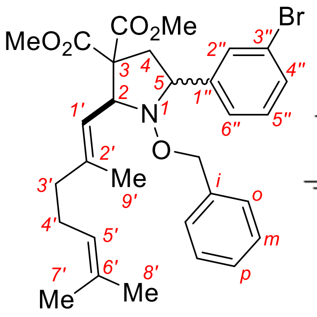


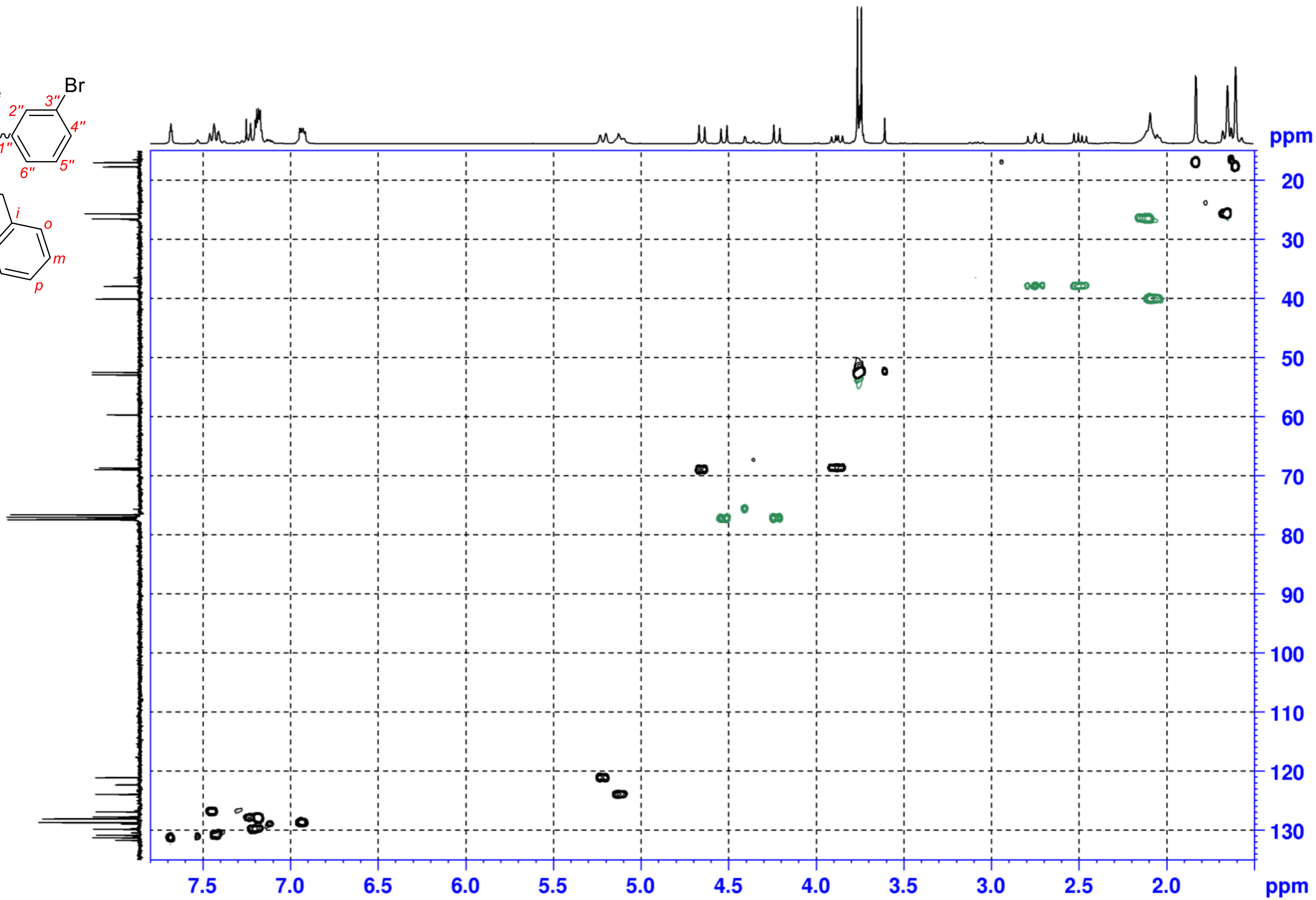

$^{13}$C NMR spectrum of *E*-**10i**, *cis*/*trans* 5.3:1 (75.5 MHz, $CDCl_3$)



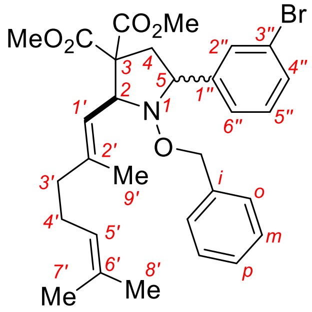




$^{1}$H,$^{1}$H-COSY NMR spectrum of *E*-**10i**, *cis*/*trans* 5.3:1 (300.1 MHz, $CDCl_3$)

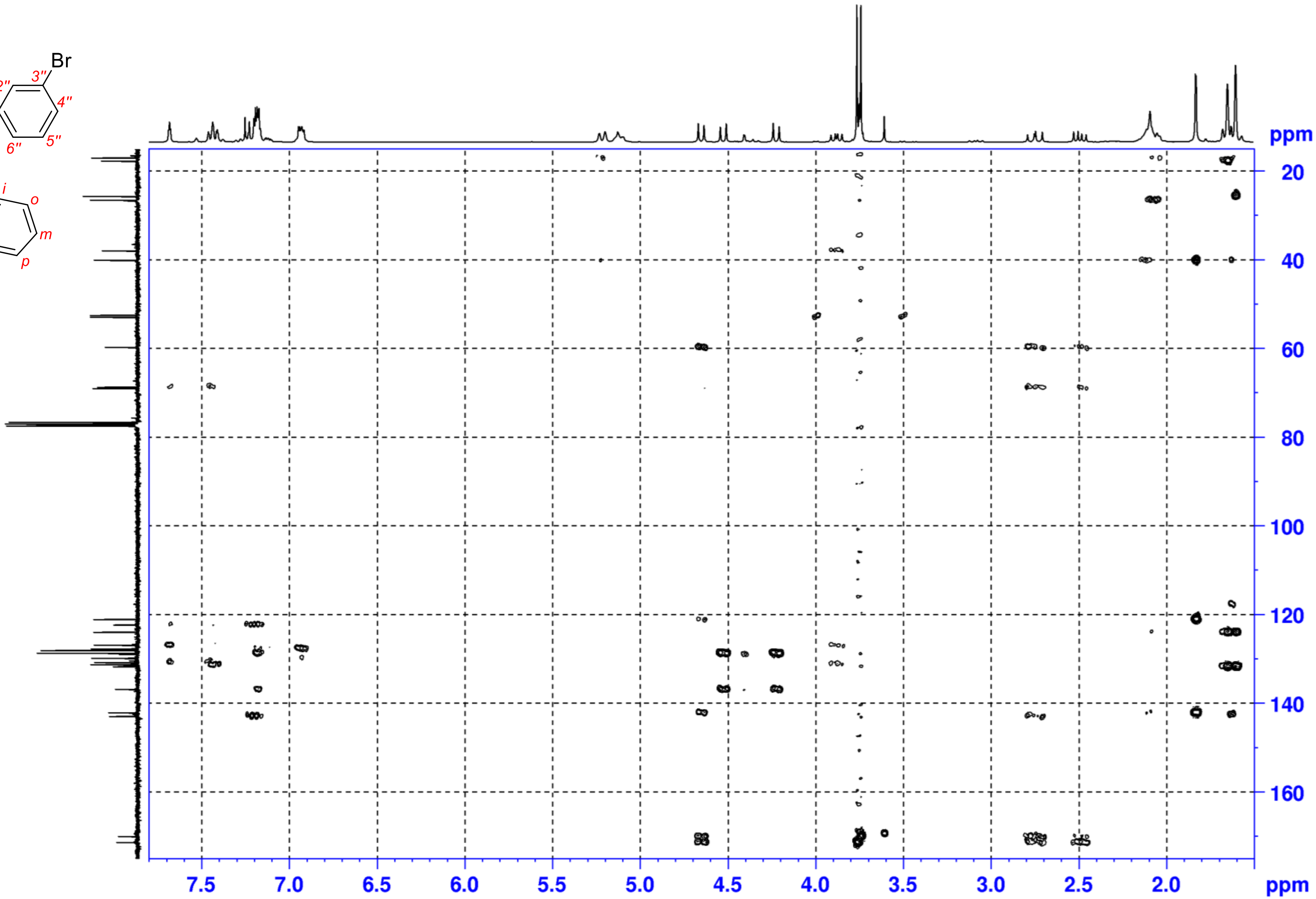



$^{1}H,^{13}C$-edited-HSQC NMR spectrum of *E*-**10i**, *cis*/*trans* 5.3:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

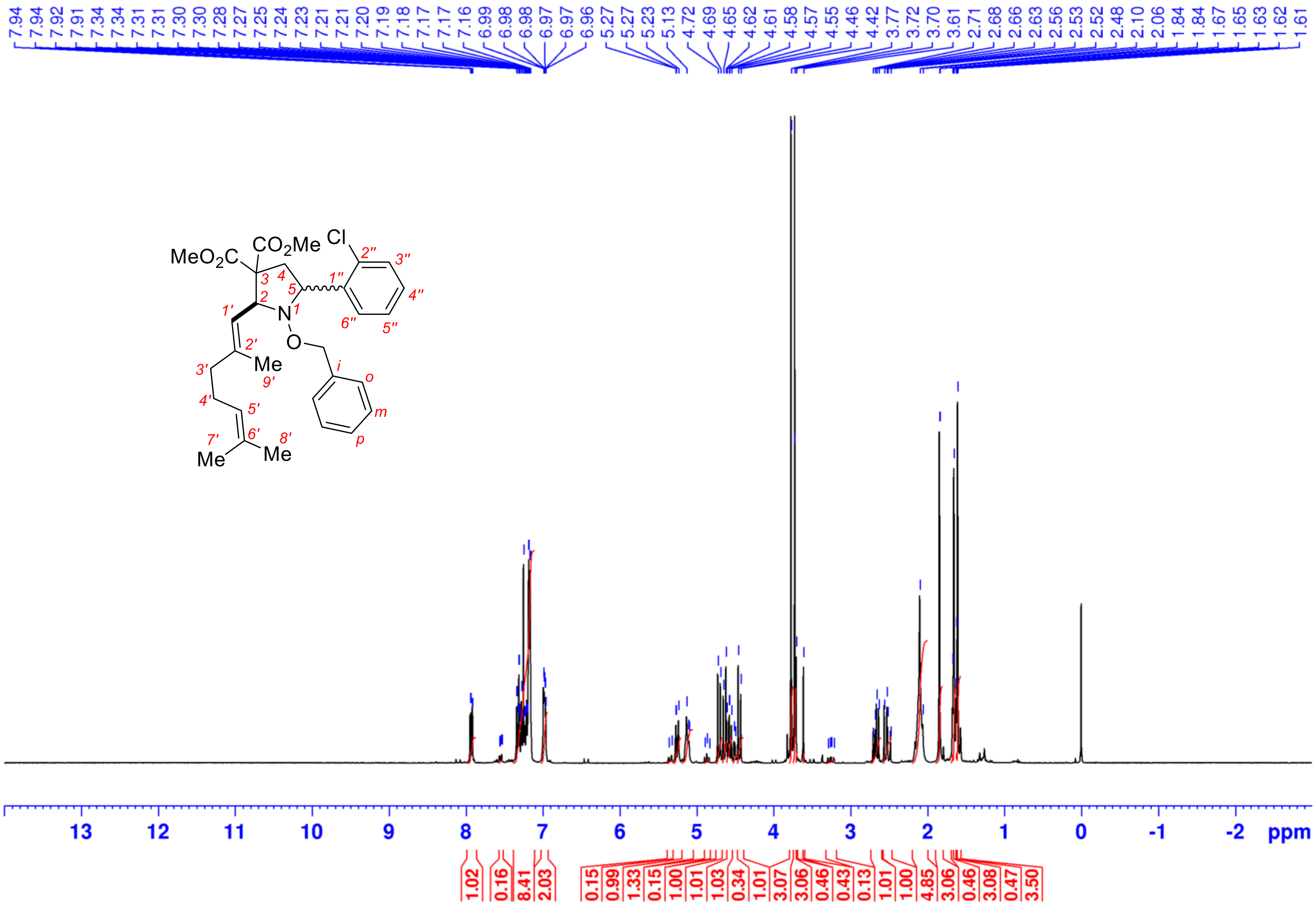




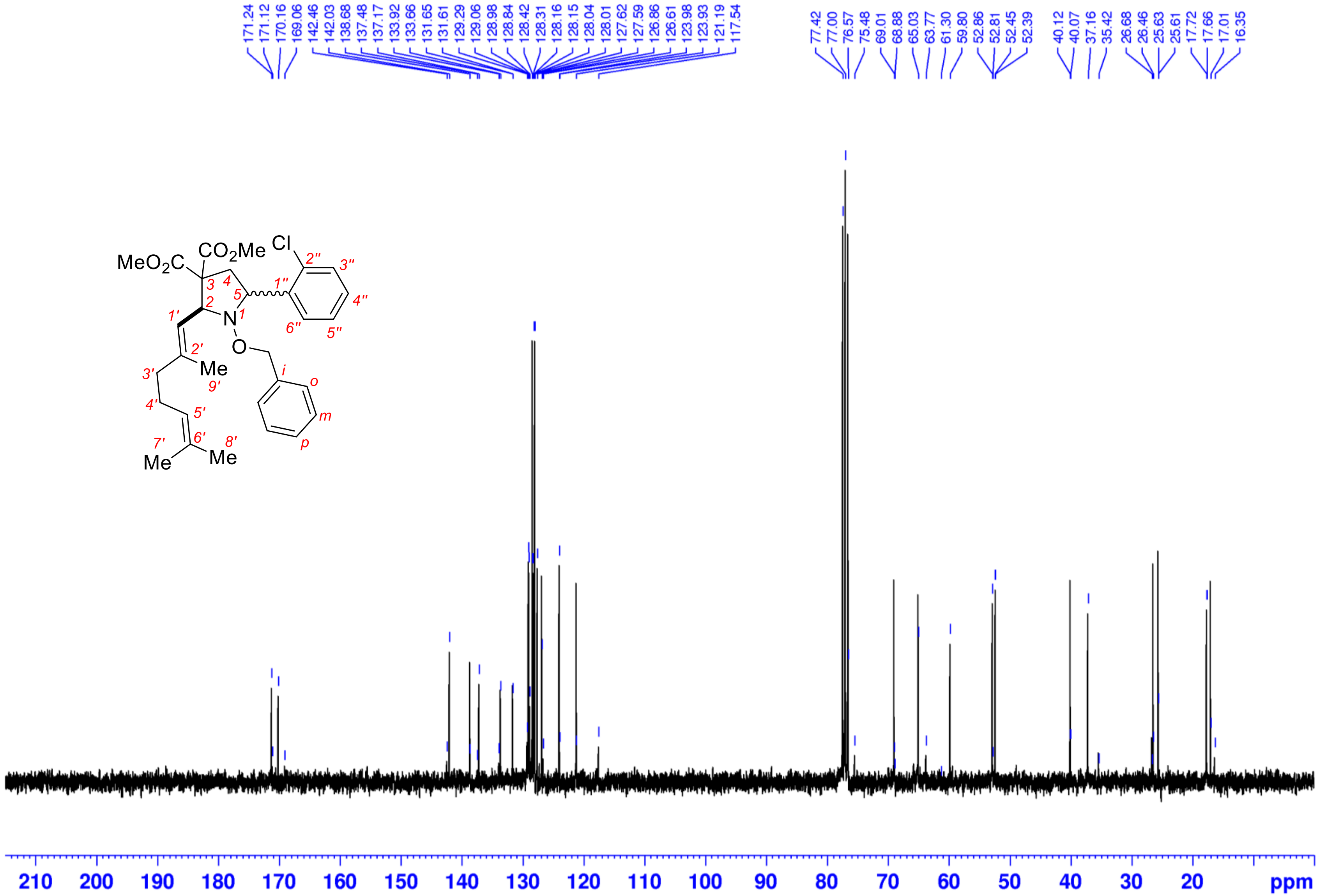




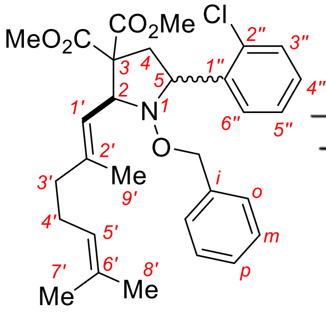
$^{1}H,^{13}C$-HMBC NMR spectrum of *E*-**10i**, *cis*/*trans* 5.3:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

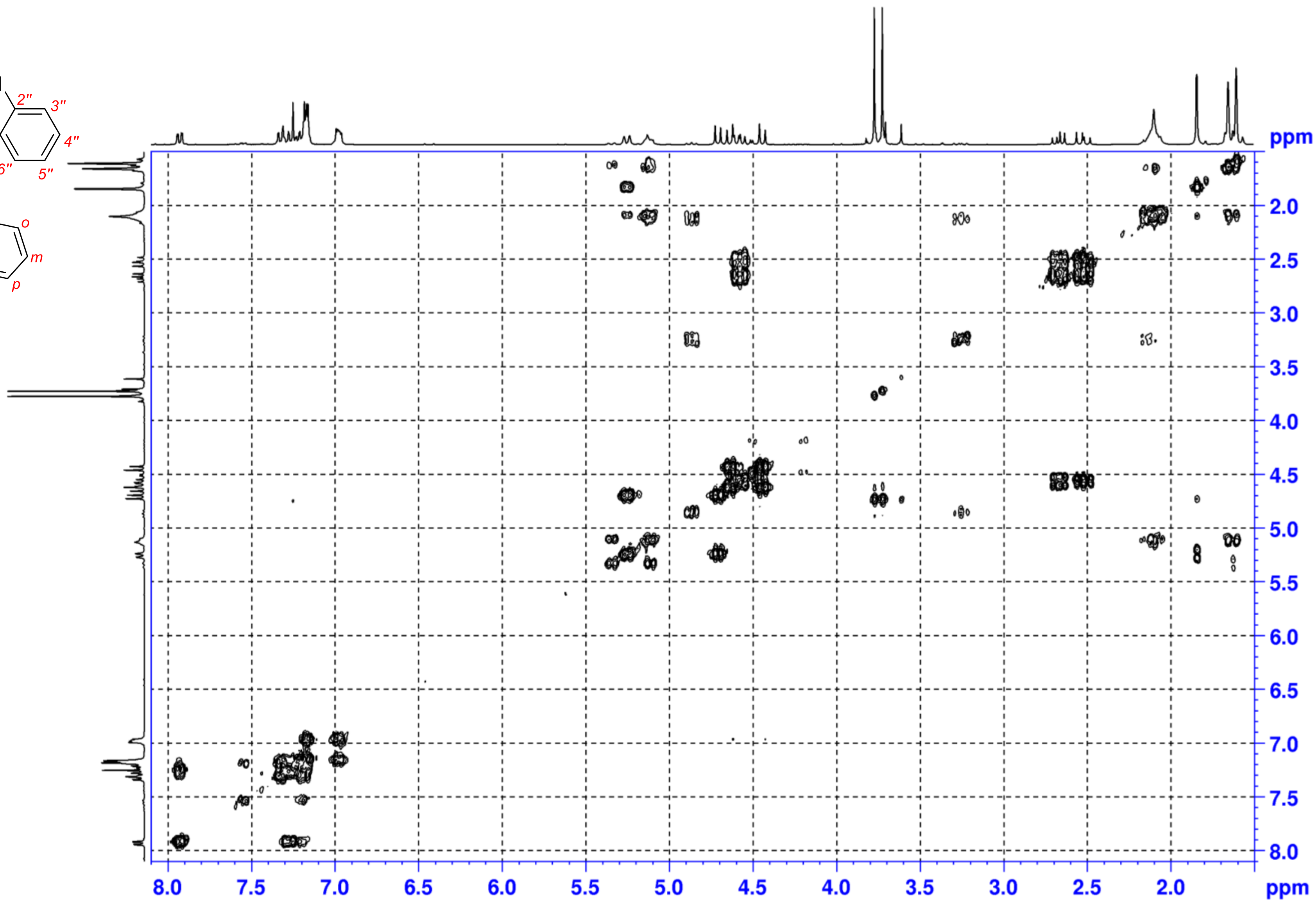


[1]H NMR spectrum of *E*-**10j**, *cis*/*trans* 6.7:1 (300.1 MHz, $CDCl_3$)

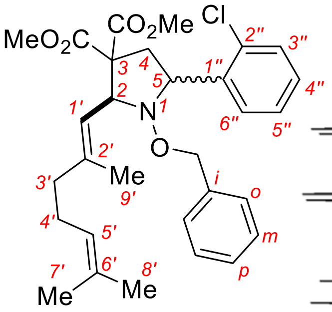


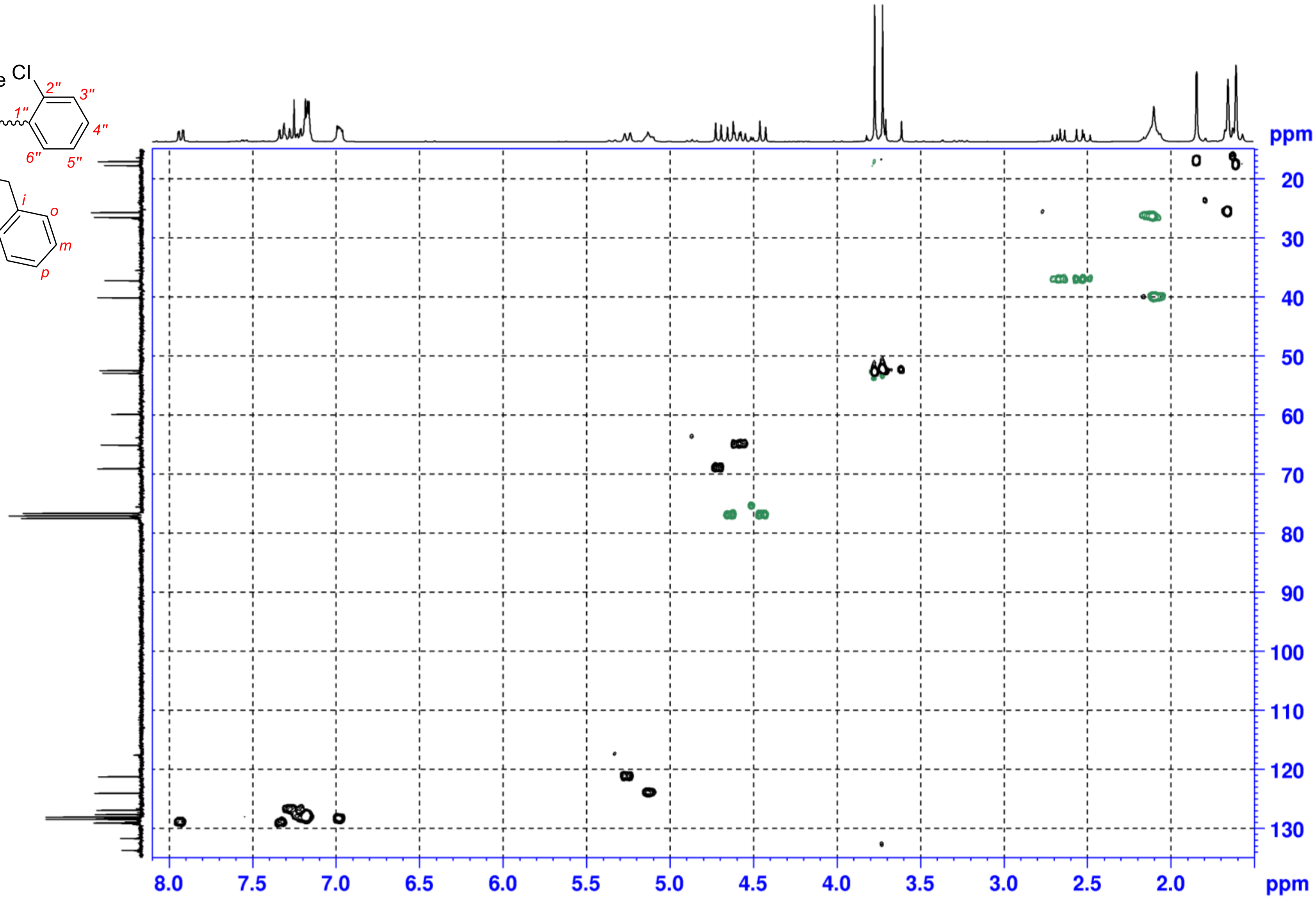

$^{13}$C NMR spectrum of *E*-**10j**, *cis*/*trans* 6.7:1 (75.5 MHz, CDCl$_3$)



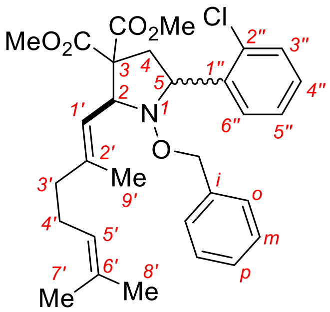



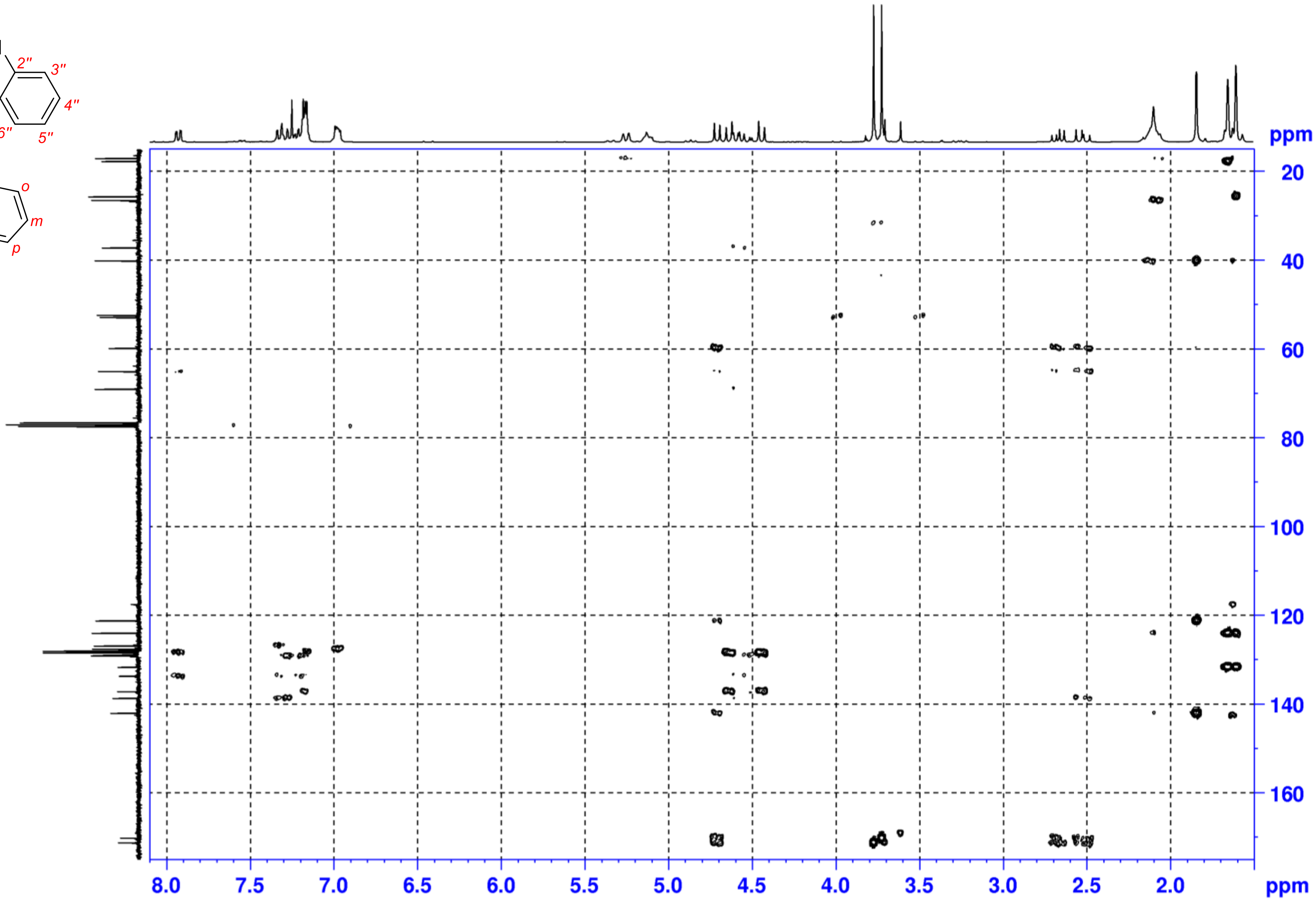

$^1H,^1H$-COSY NMR spectrum of *E*-**10j**, *cis*/*trans* 6.7:1 (300.1 MHz, $CDCl_3$)



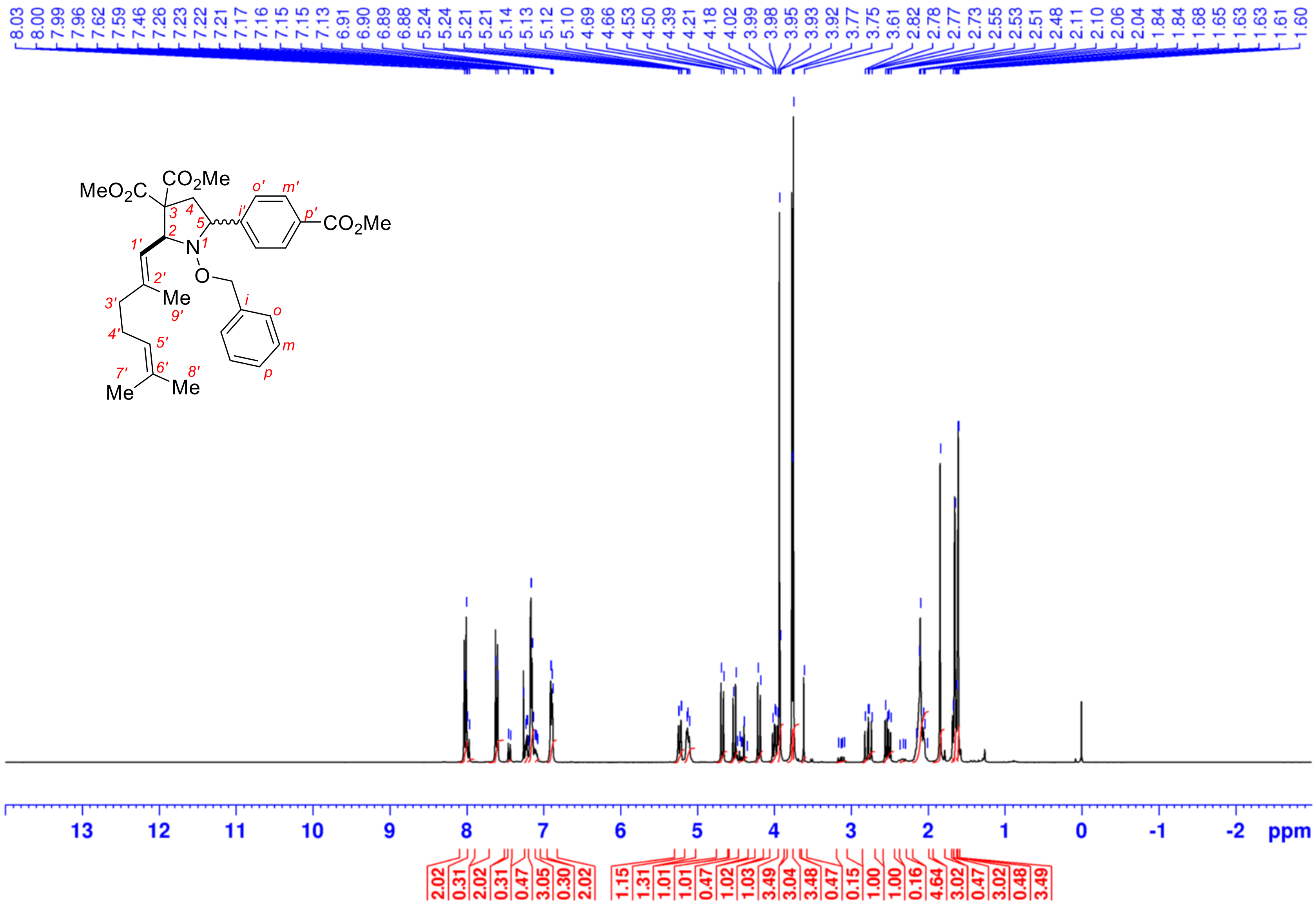




[1]H,[13]C-edited-HSQC NMR spectrum of *E*-**10j**, *cis*/*trans* 6.7:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

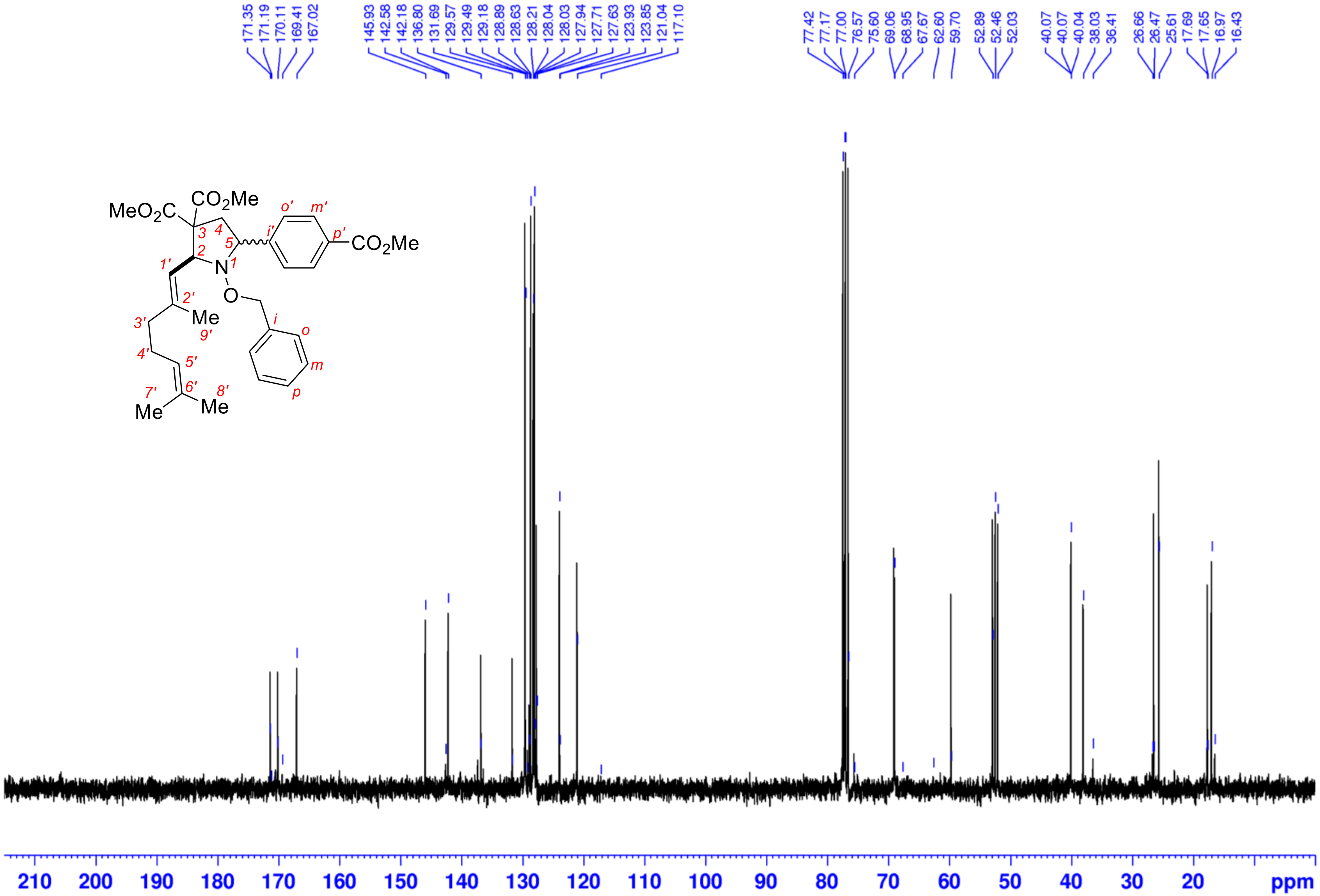


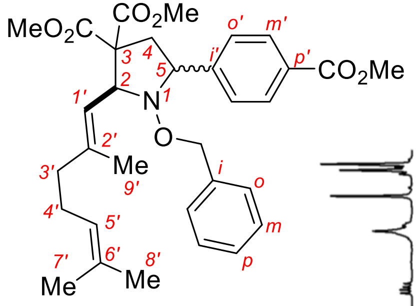

$^{1}H,^{13}C$-HMBC NMR spectrum of *E*-**10j**, *cis*/*trans* 6.7:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

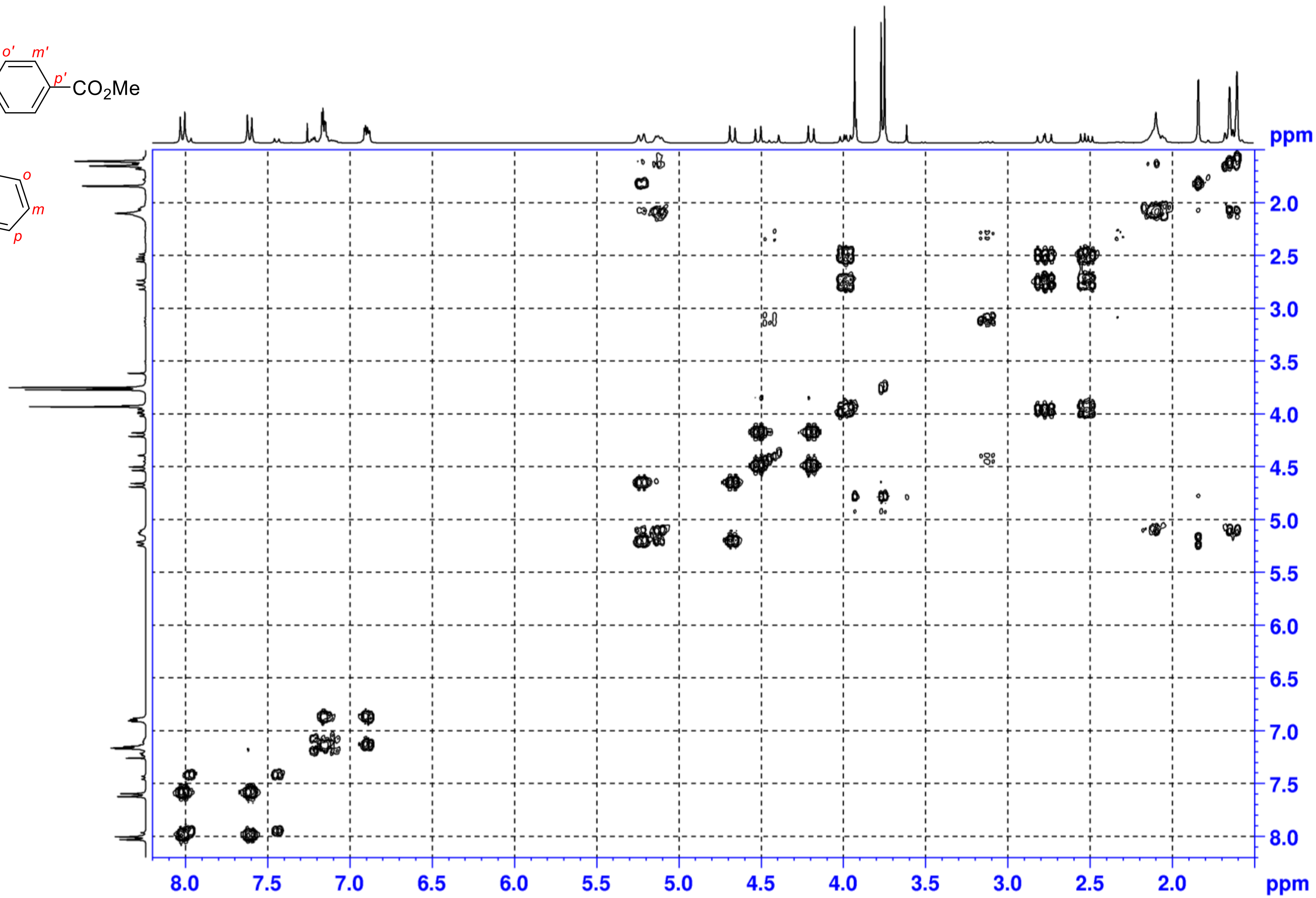


[1]H NMR spectrum of *E*-**10k**, *cis*/*trans* 6.8:1 (300.1 MHz, $CDCl_3$)

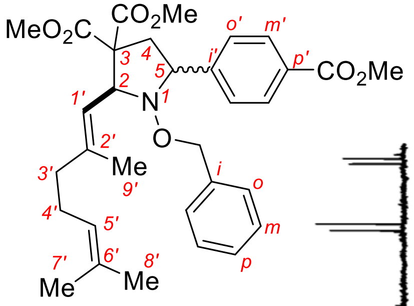


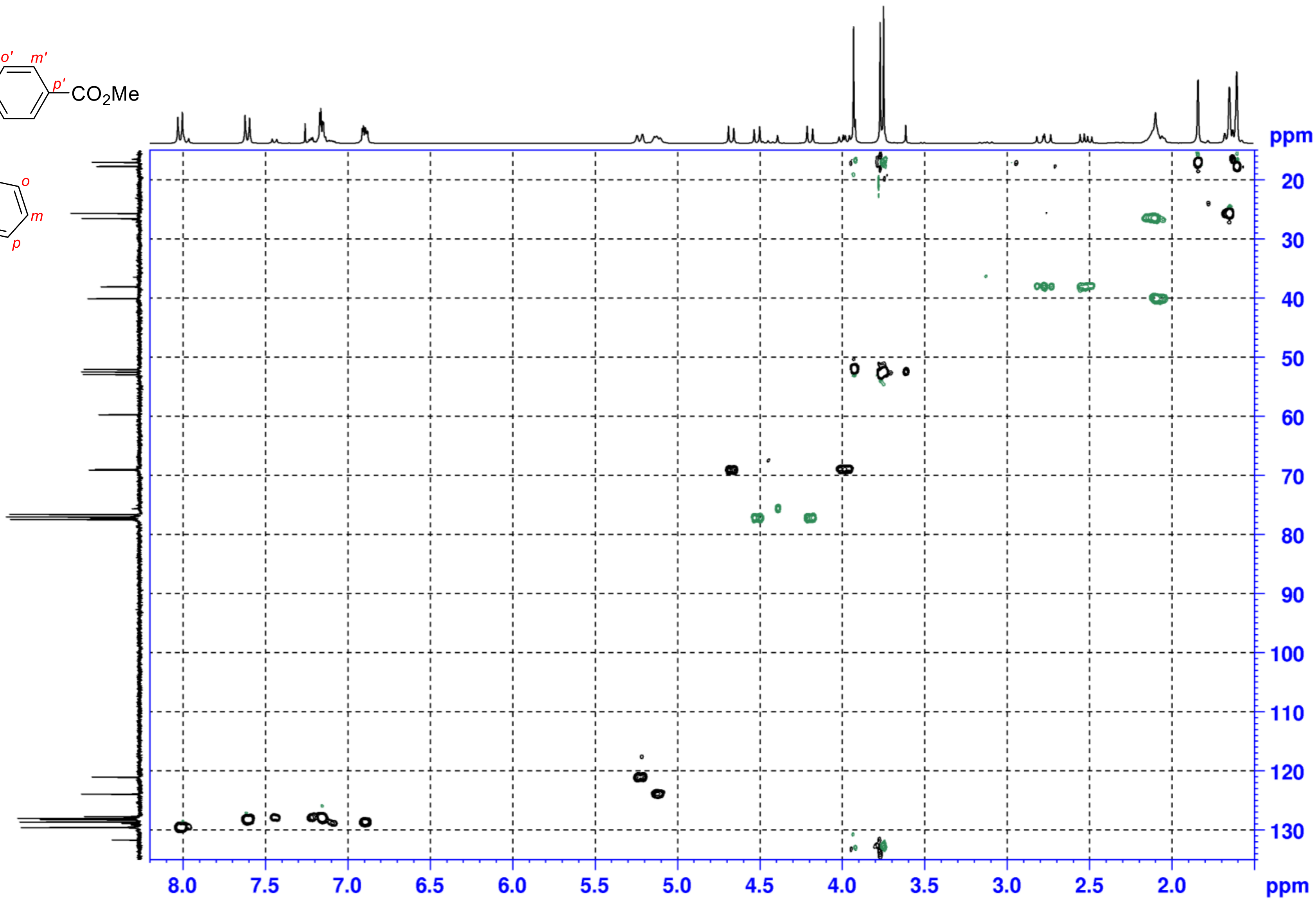
$^{13}$C NMR spectrum of *E*-**10k**, *cis*/*trans* 6.8:1 (75.5 MHz, $CDCl_3$)



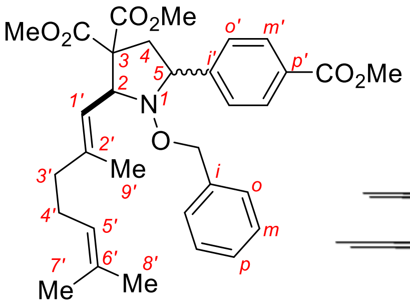



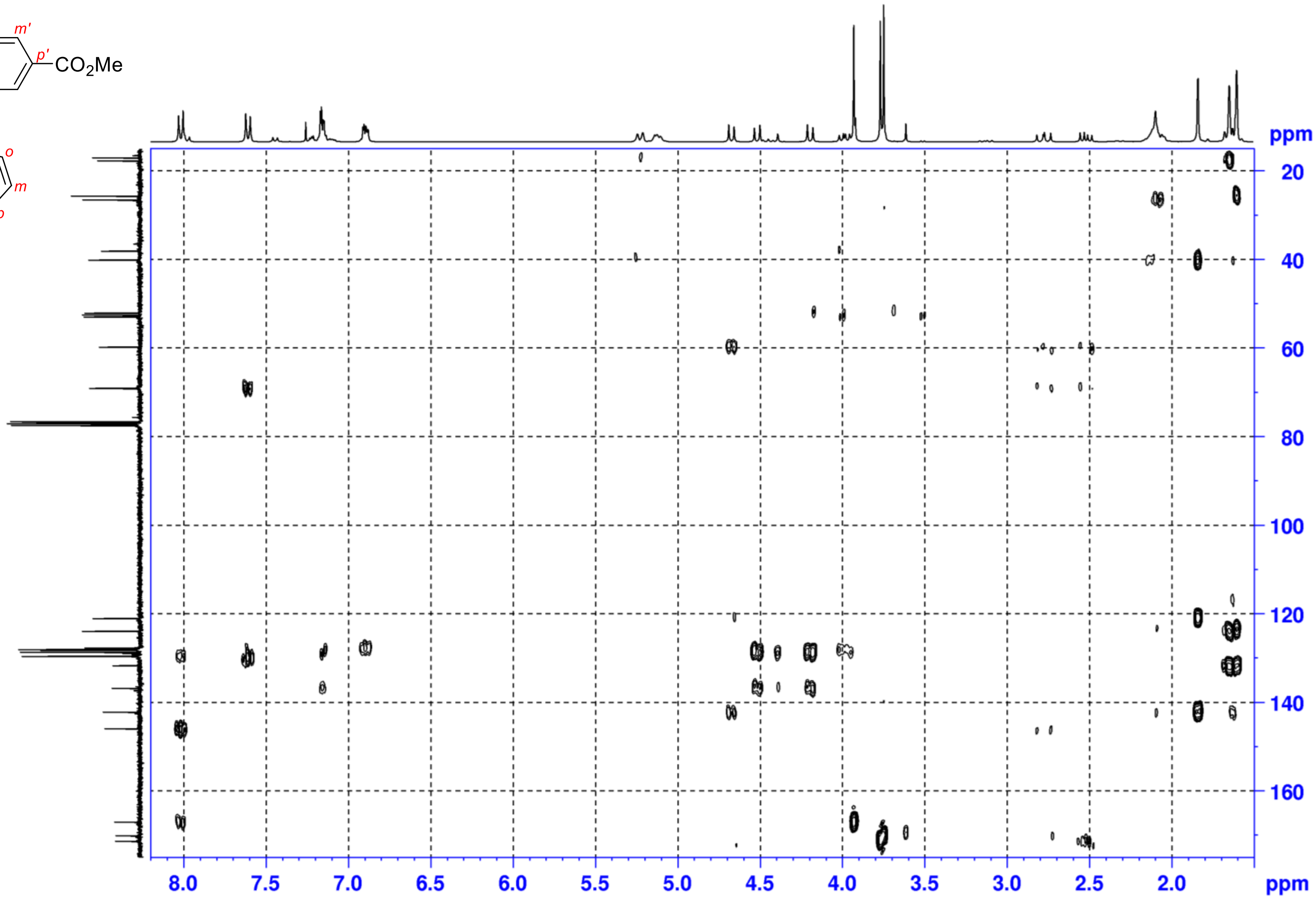

[1]H,[1]H-COSY NMR spectrum of *E*-**10k**, *cis*/*trans* 6.8:1 (300.1 MHz, $CDCl_3$)



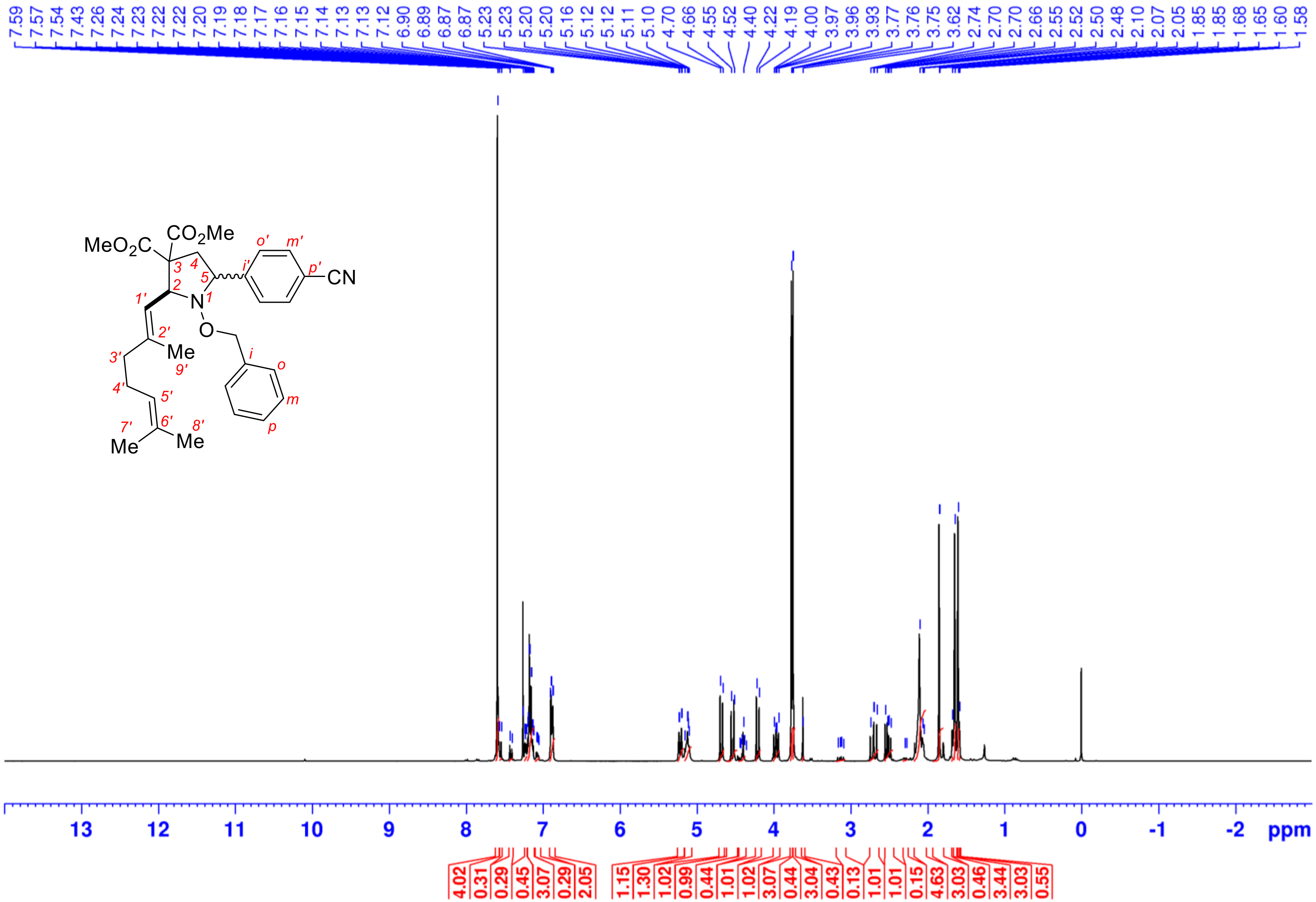




$^{1}H,^{13}C$-edited-HSQC NMR spectrum of *E*-**10k**, *cis*/*trans* 6.8:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

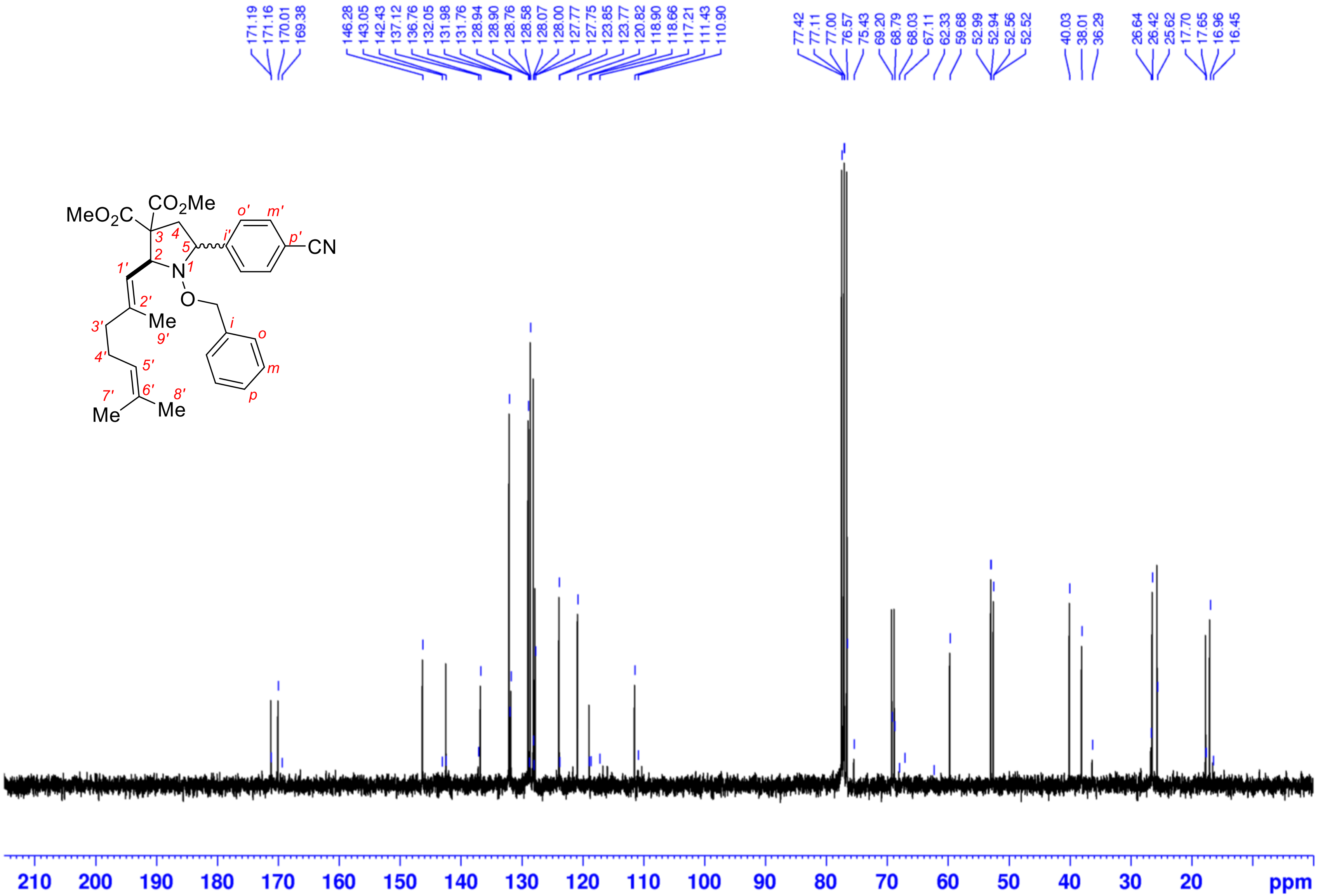


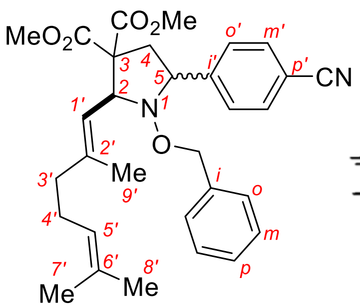

[1]H,[13]C-HMBC NMR spectrum of *E*-**10k**, *cis*/*trans* 6.8:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

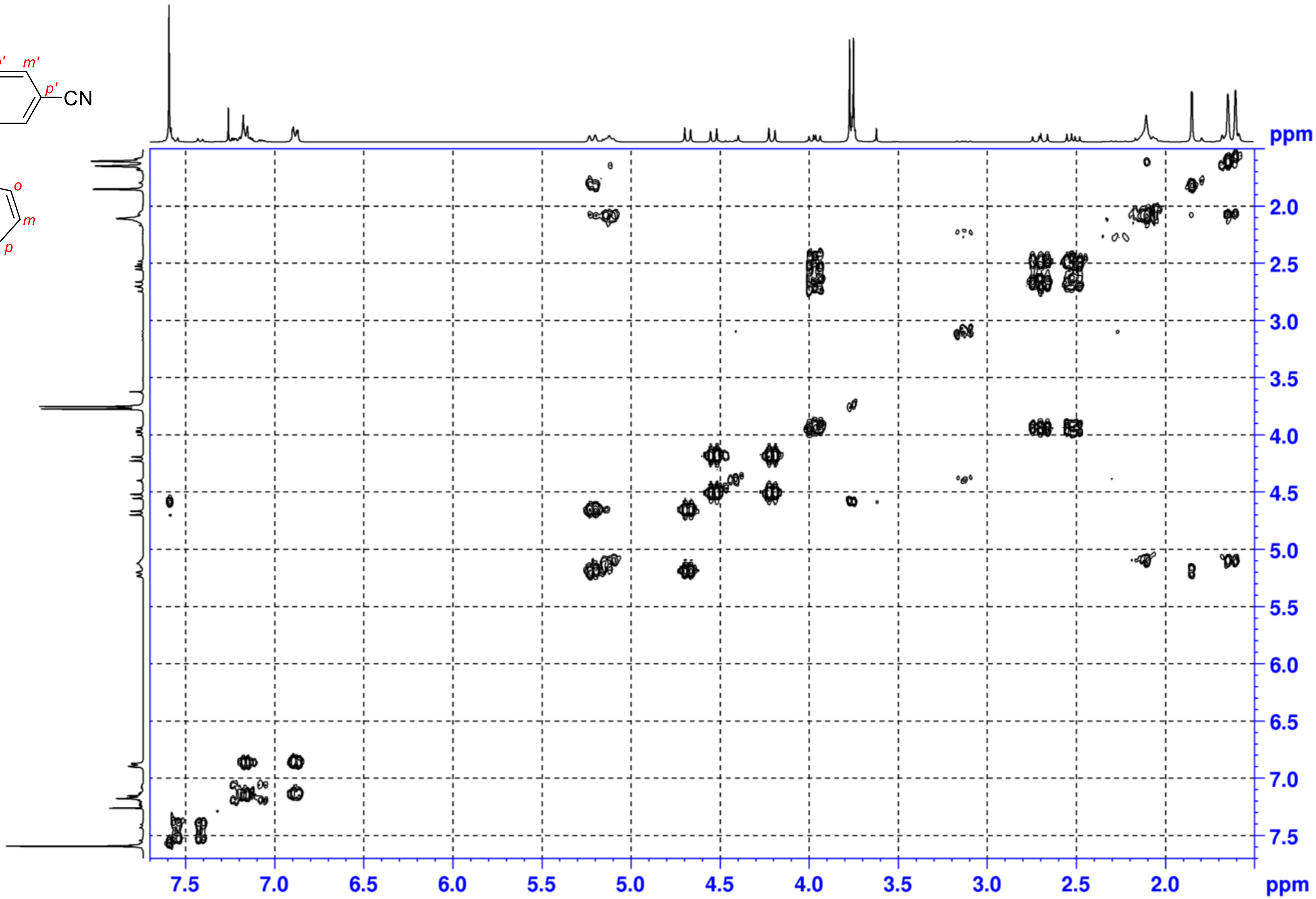


[1]H NMR spectrum of *E*-**10l**, *cis*/*trans* 7.5:1 (300.1 MHz, $CDCl_3$)

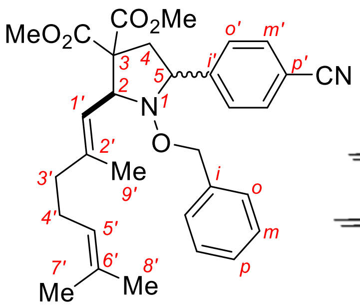


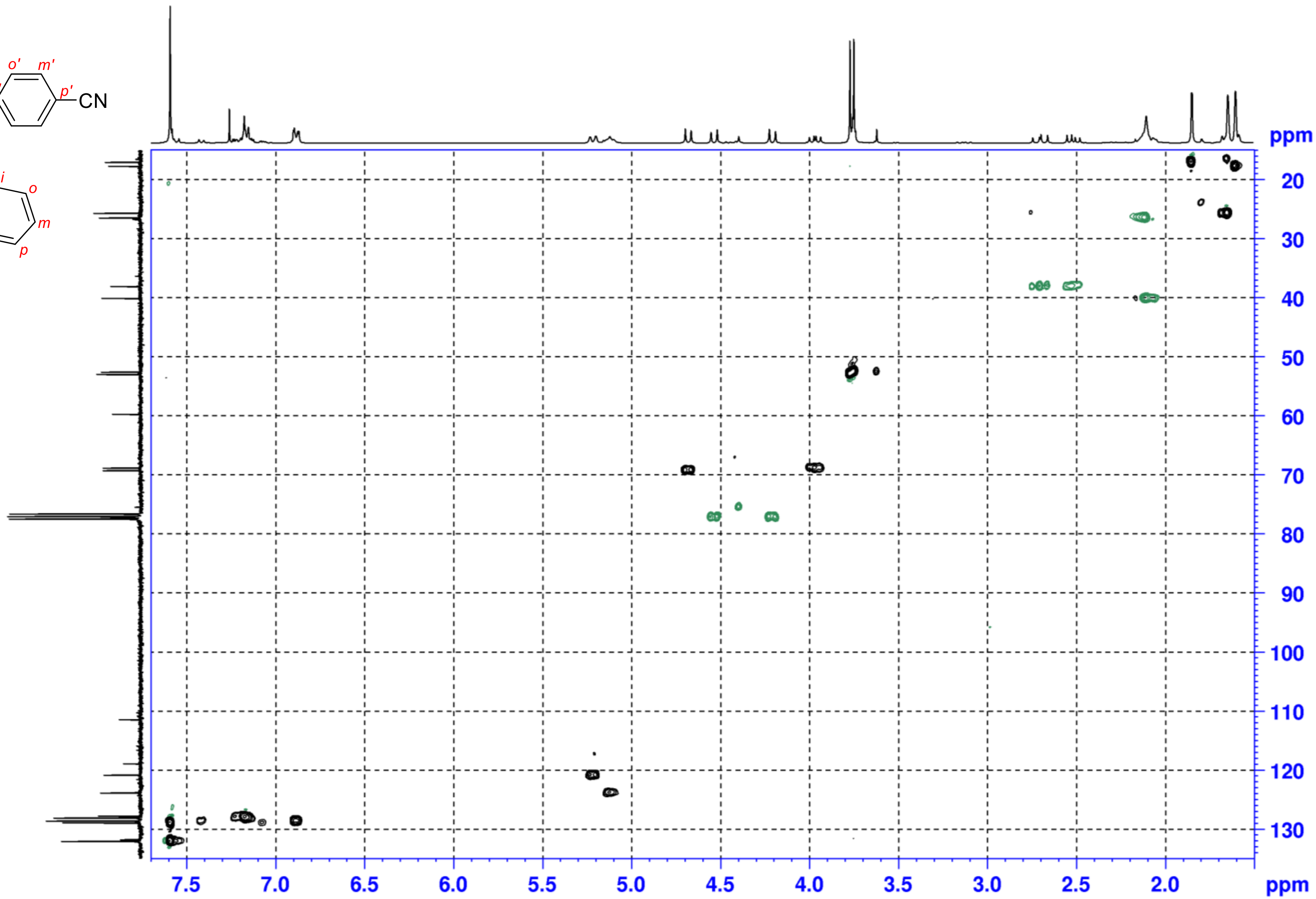

$^{13}$C NMR spectrum of *E*-**10l**, *cis*/*trans* 7.5:1 (75.5 MHz, $CDCl_3$)



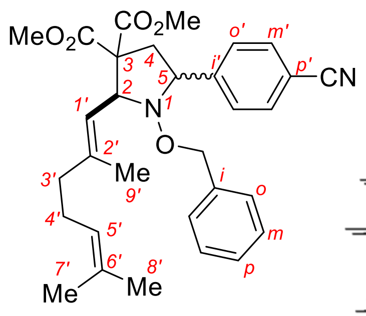


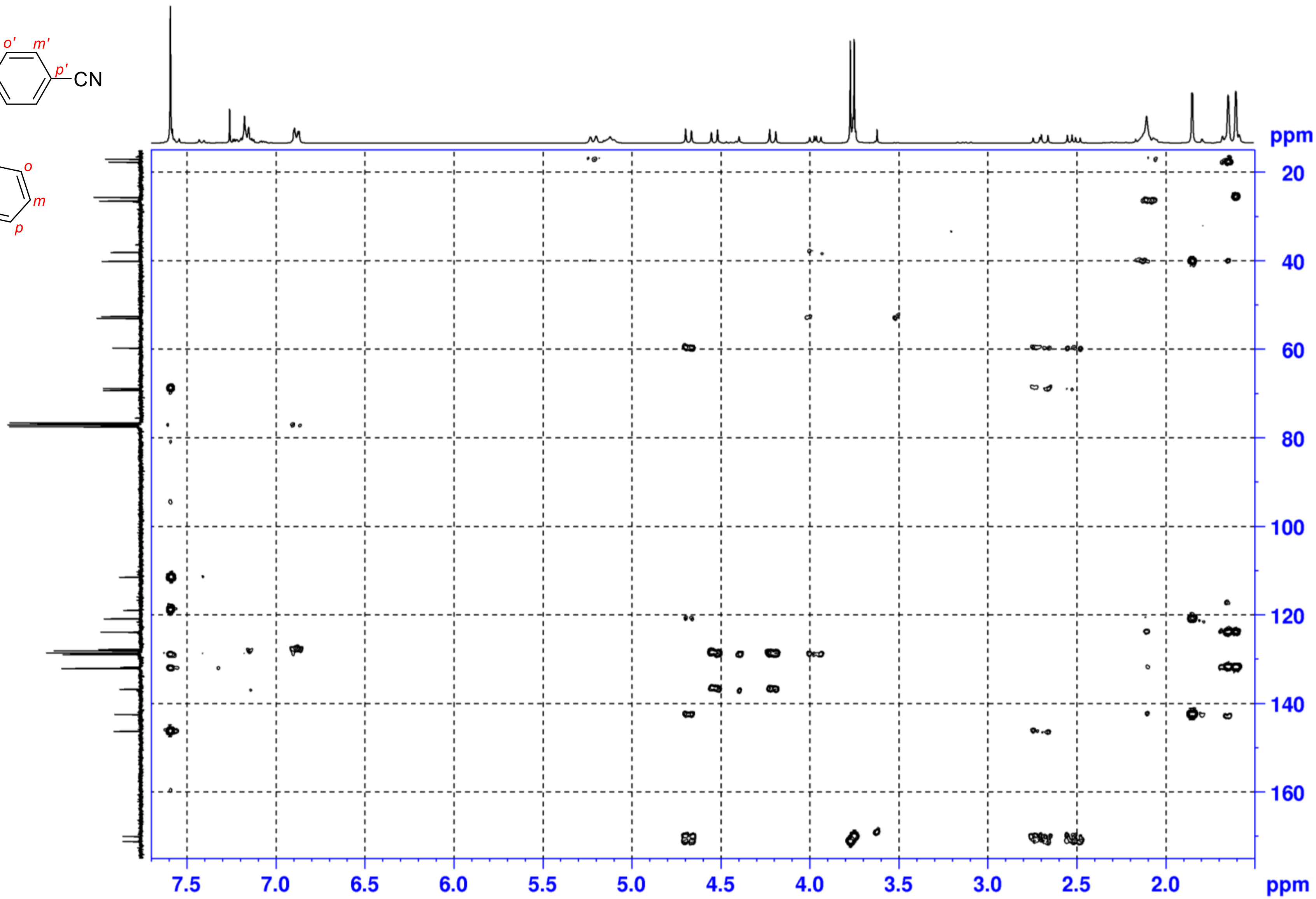
$^1H,^1H$-COSY NMR spectrum of *E*-**10l**, *cis*/*trans* 7.5:1 (300.1 MHz, $CDCl_3$)



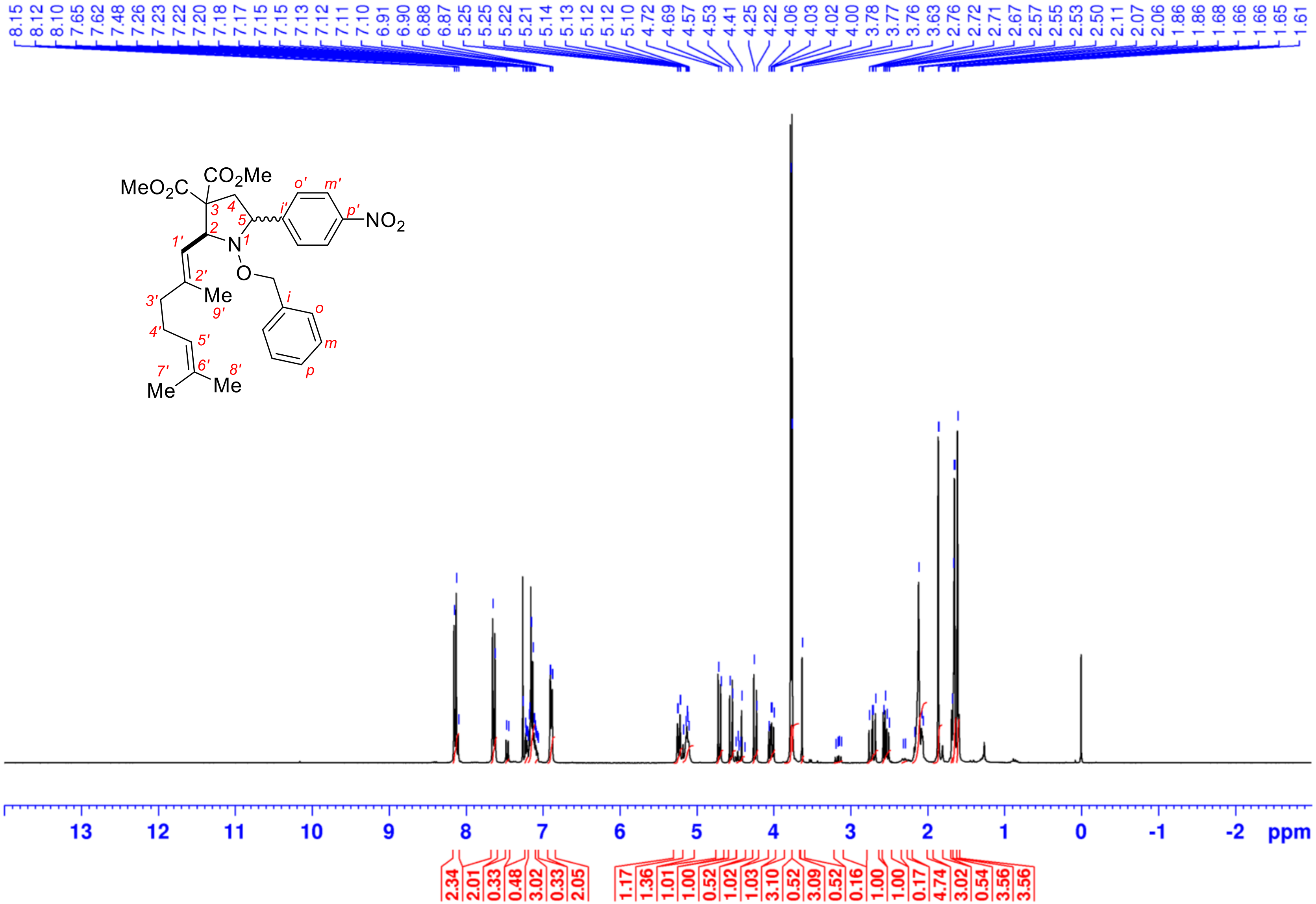



$^{1}$H,$^{13}$C-edited-HSQC NMR spectrum of *E*-**10l**, *cis*/*trans* 7.5:1 ($^{1}$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)

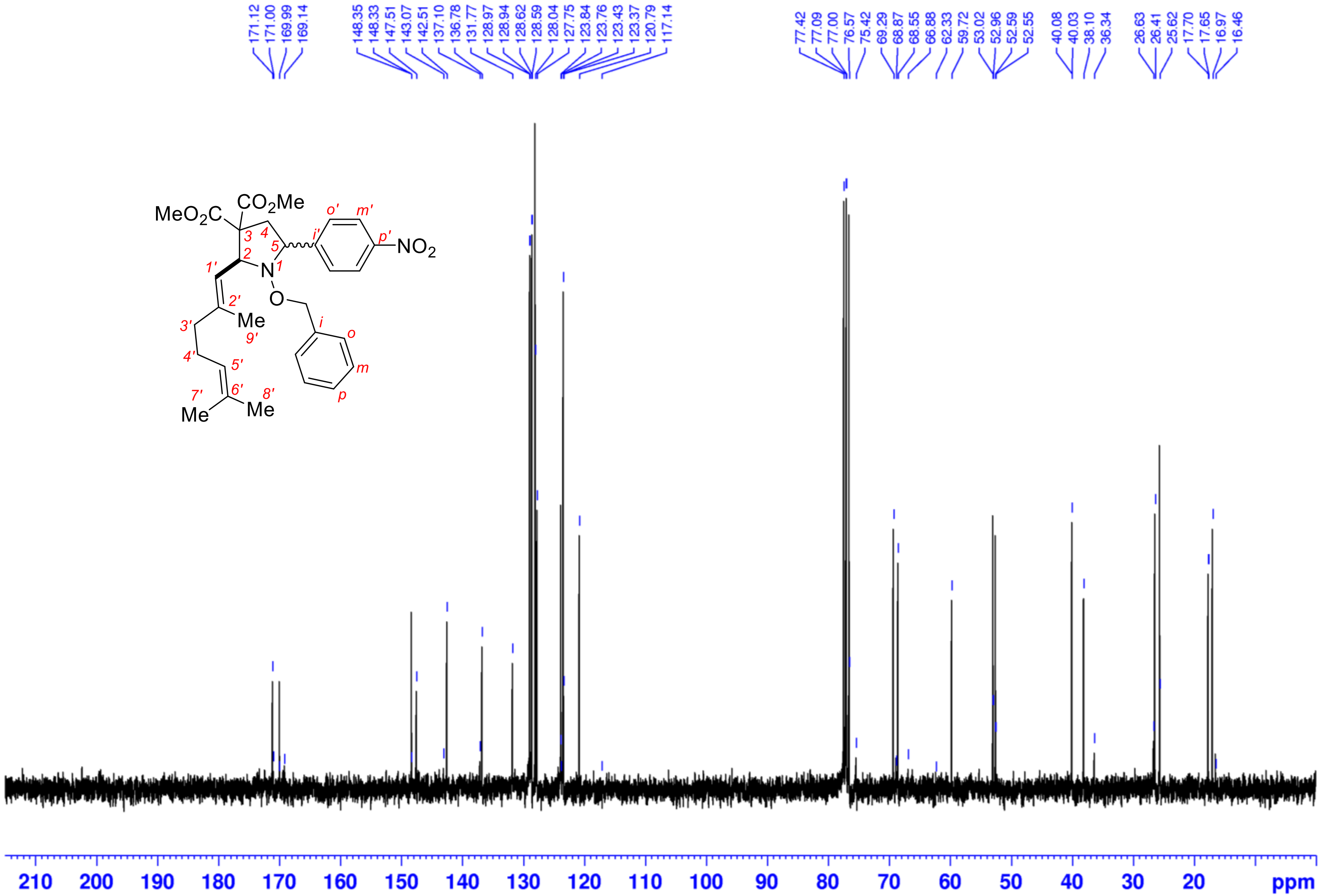




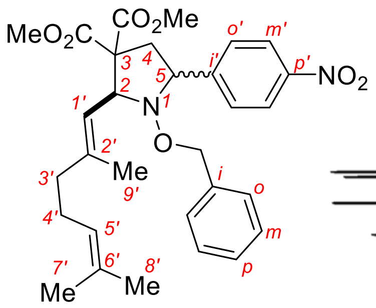
[1]H,[13]C-HMBC NMR spectrum of *E*-**10l**, *cis*/*trans* 7.5:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

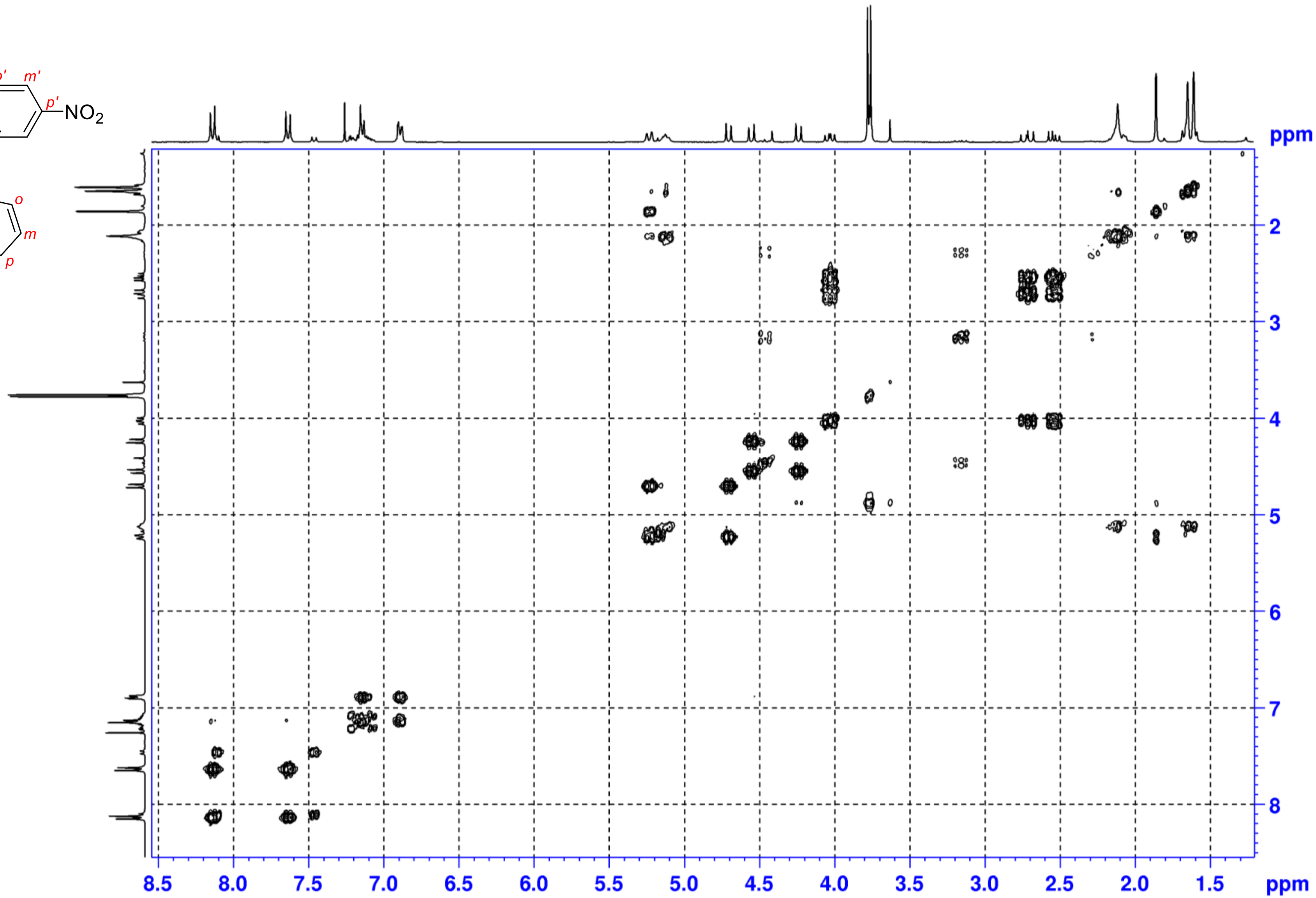


[1]H NMR spectrum of *E*-**10m**, *cis*/*trans* 6.3:1 (300.1 MHz, $CDCl_3$)

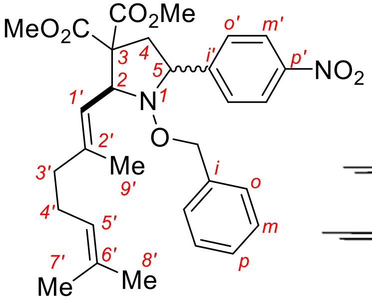


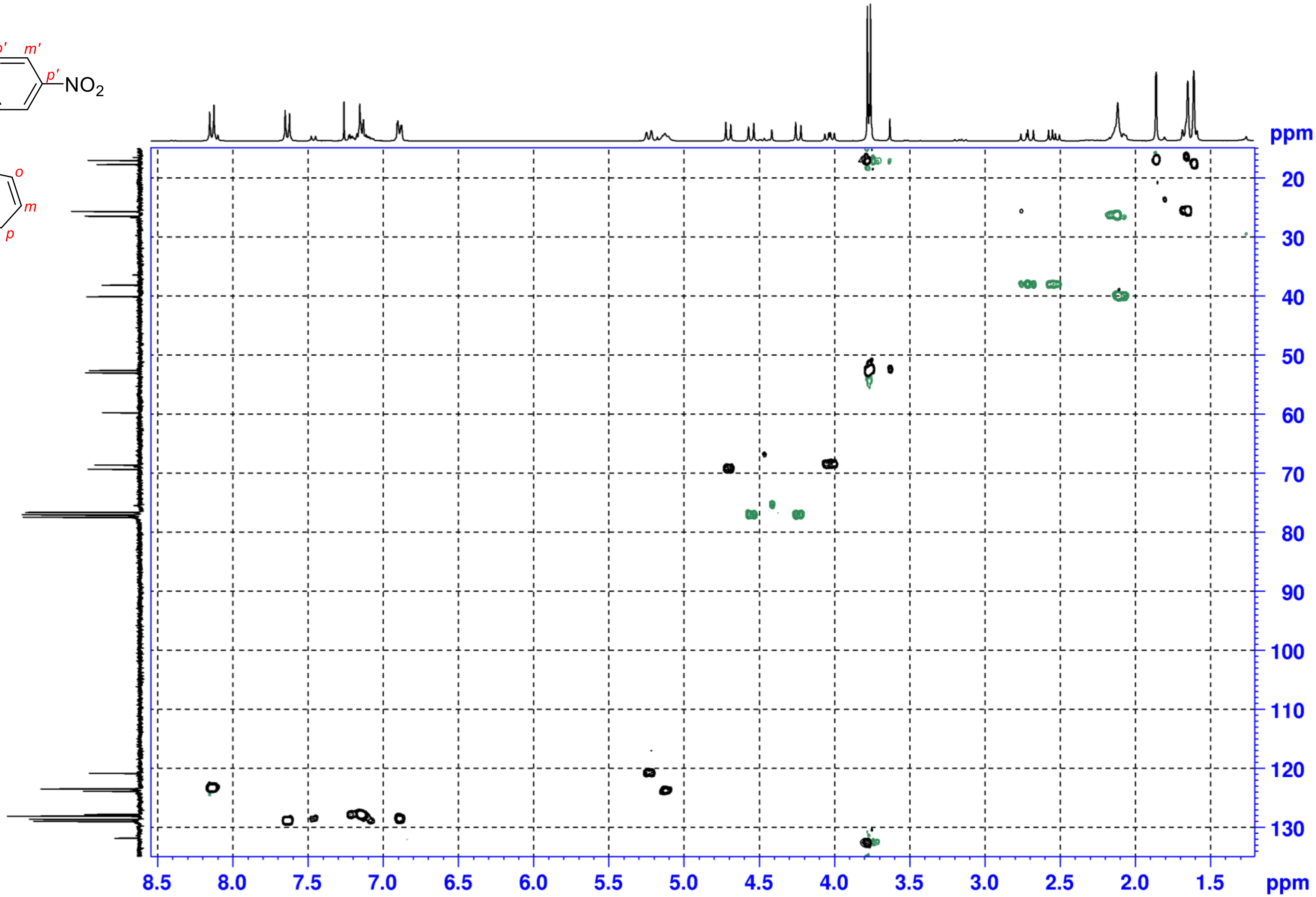

$^{13}$C NMR spectrum of *E*-**10m**, *cis*/*trans* 6.3:1 (75.5 MHz, $CDCl_3$)



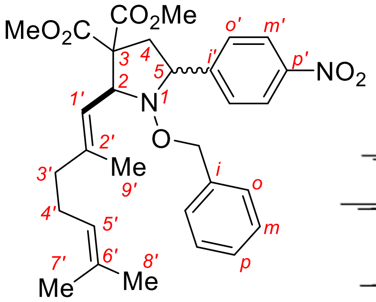



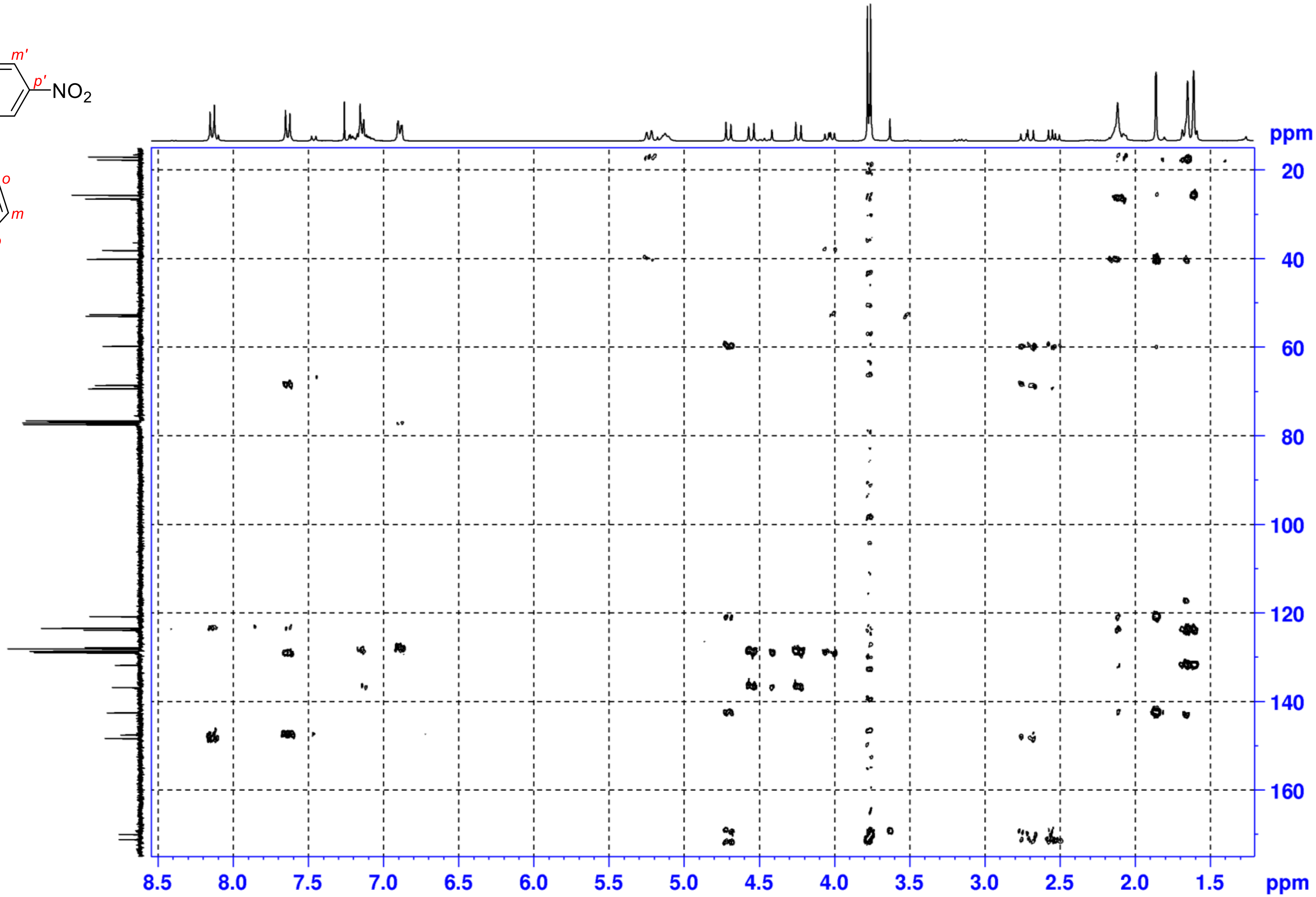
[1]H,[1]H-COSY NMR spectrum of *E*-**10m**, *cis*/*trans* 6.3:1 (300.1 MHz, $CDCl_3$)



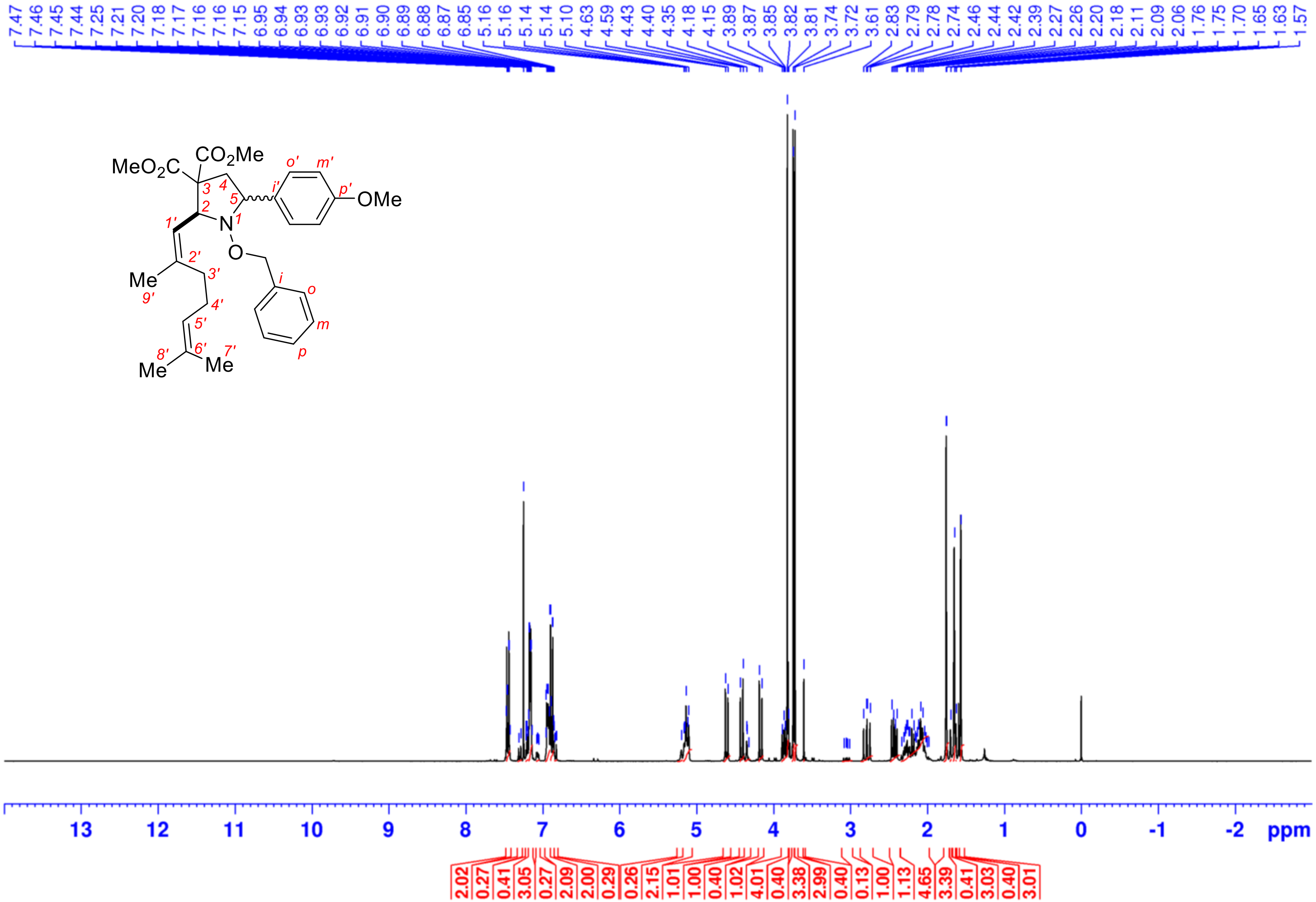


[1]H,[13]C-edited-HSQC NMR spectrum of *E*-**10m**, *cis*/*trans* 6.3:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

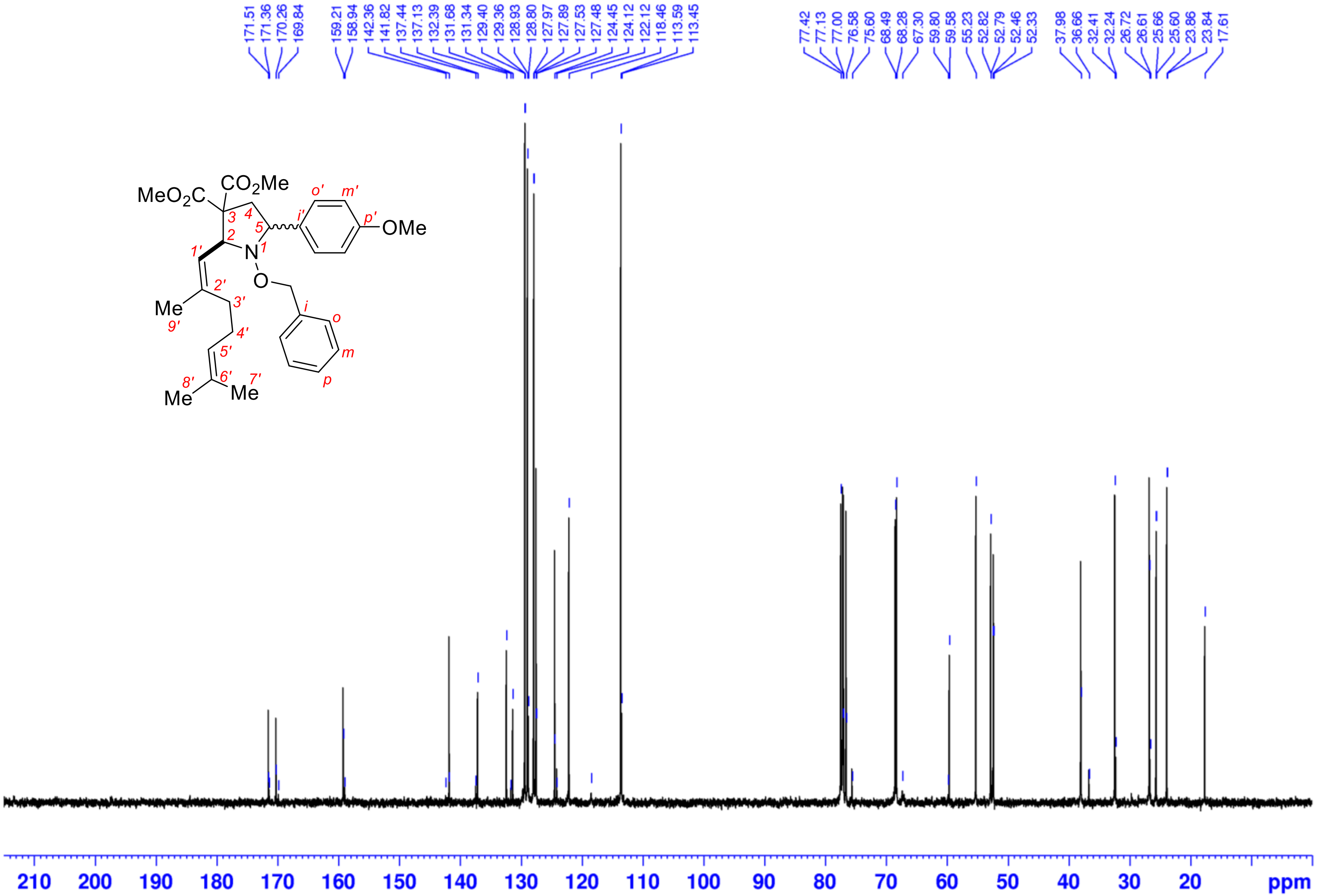


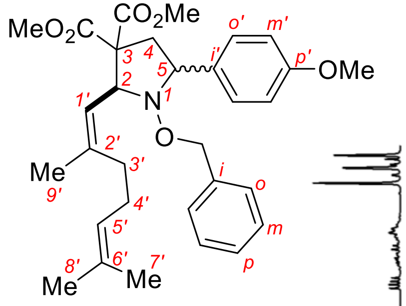

$^{1}H,^{13}C$-HMBC NMR spectrum of *E*-**10m**, *cis*/*trans* 6.3:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

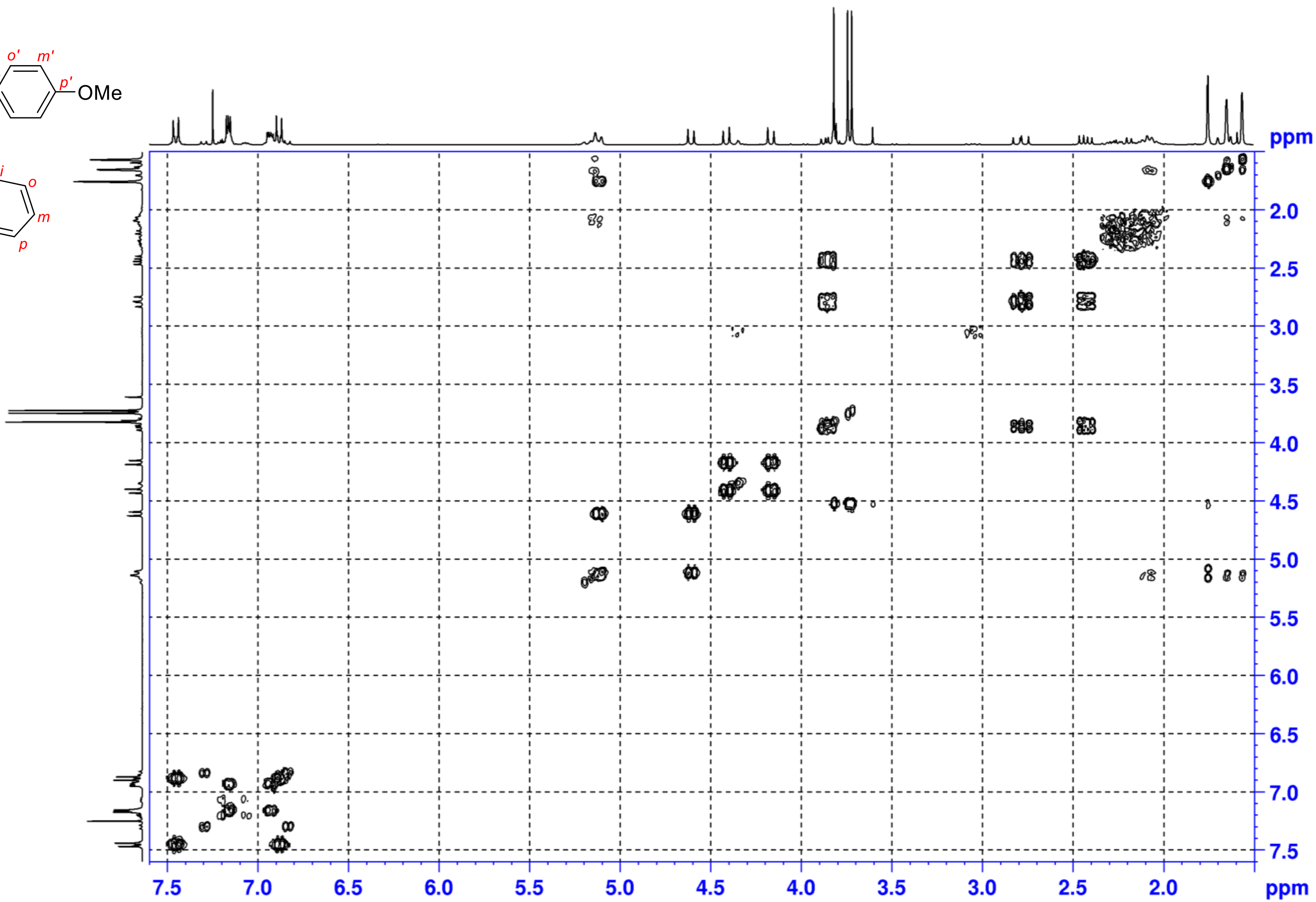


[1]H NMR spectrum of *Z*-**10a**, *cis*/*trans* 7.7:1 (300.1 MHz, $CDCl_3$)

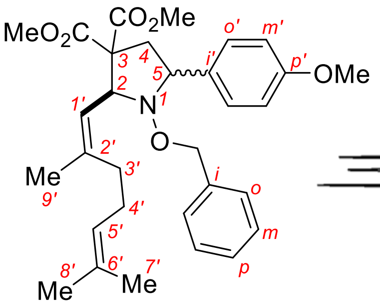


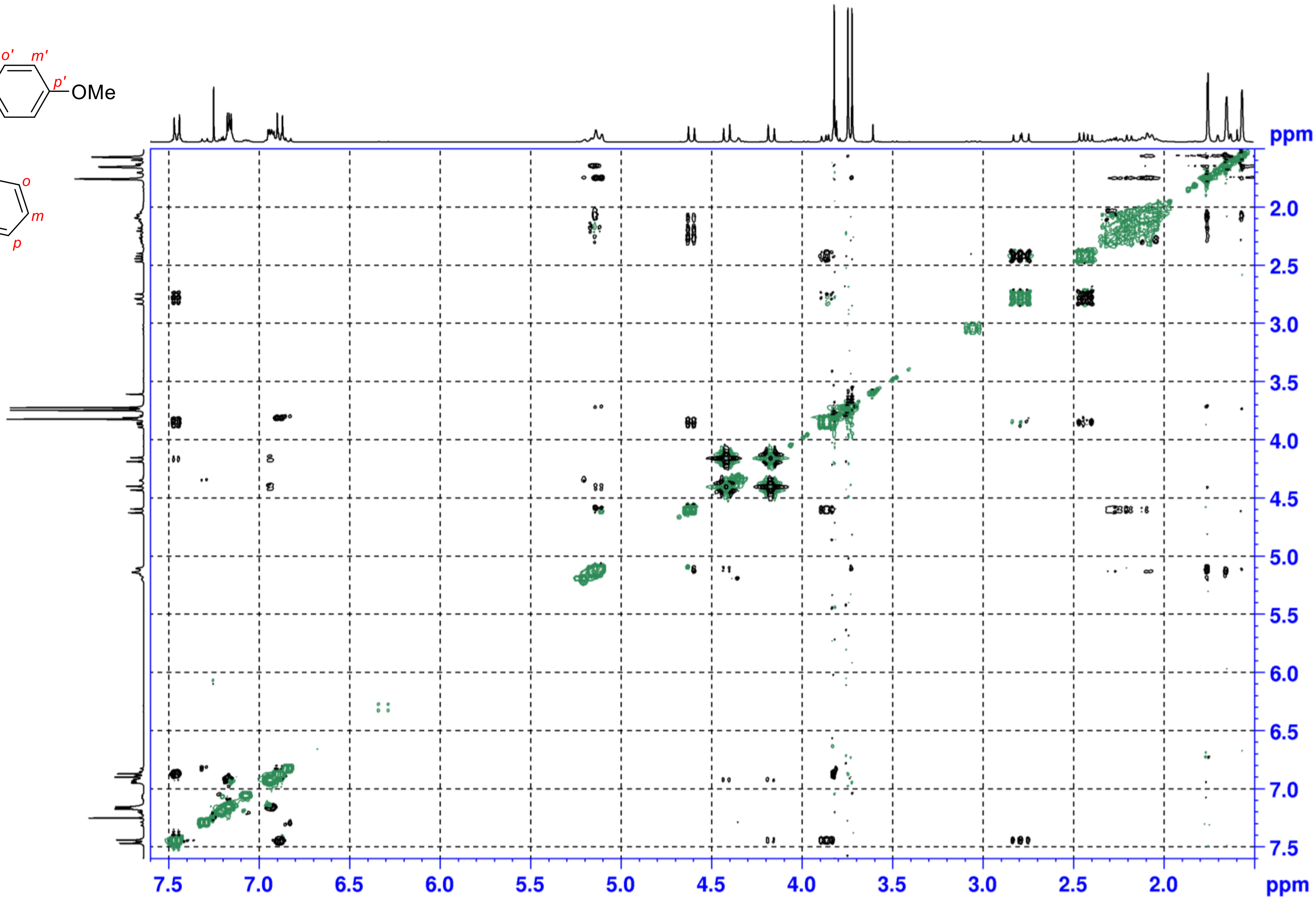

$^{13}$C NMR spectrum of *Z*-**10a**, *cis*/*trans* 7.7:1 (75.5 MHz, $CDCl_3$)



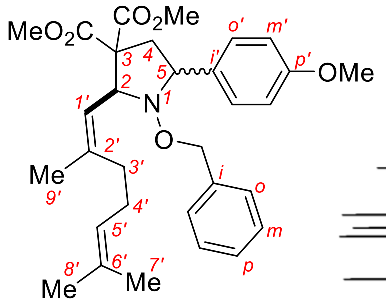



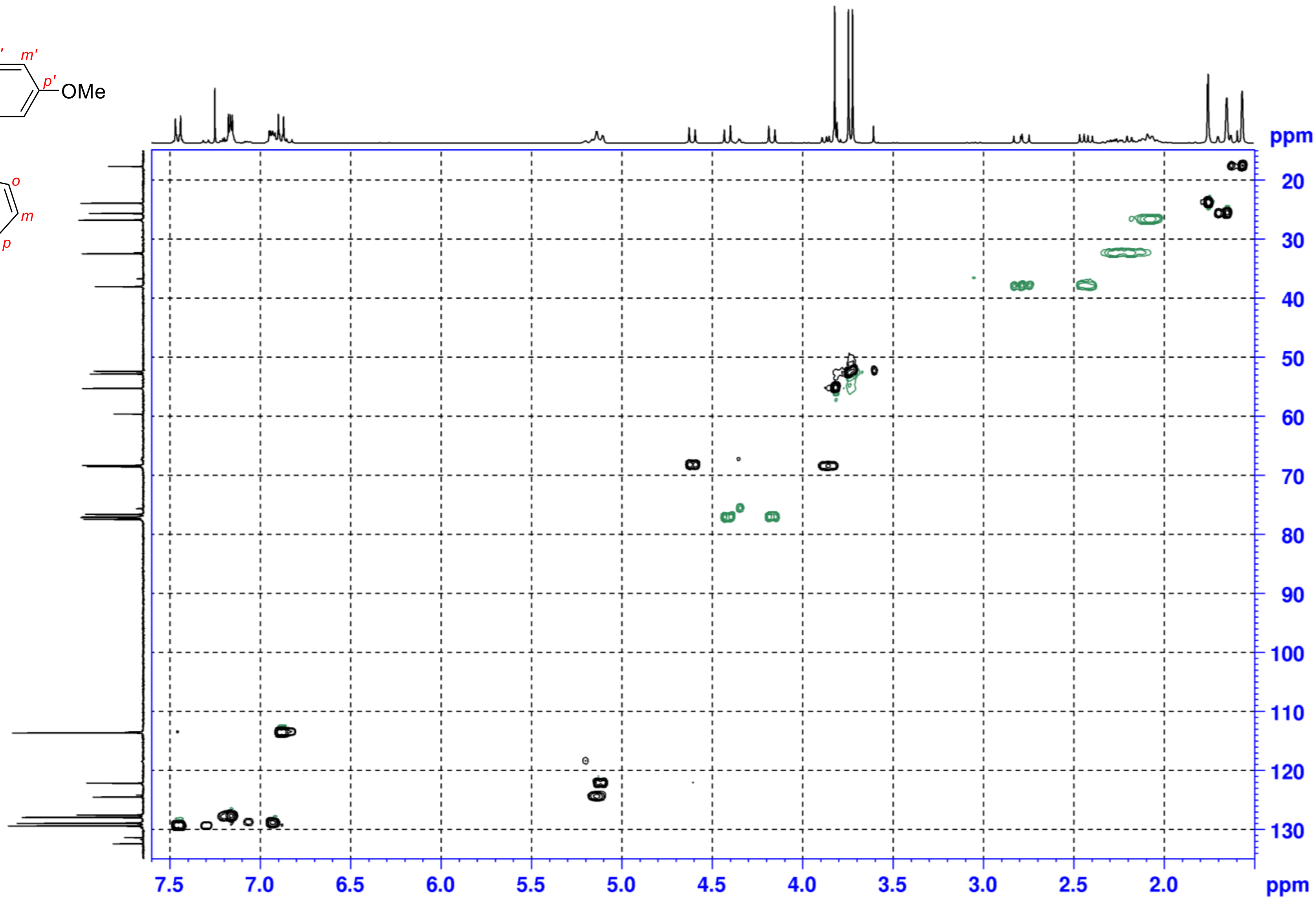

[1]H,[1]H-COSY NMR spectrum of *Z*-**10a**, *cis*/*trans* 7.7:1 (300.1 MHz, $CDCl_3$)



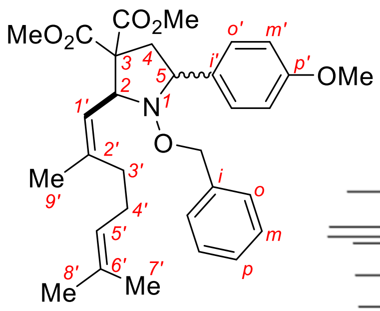



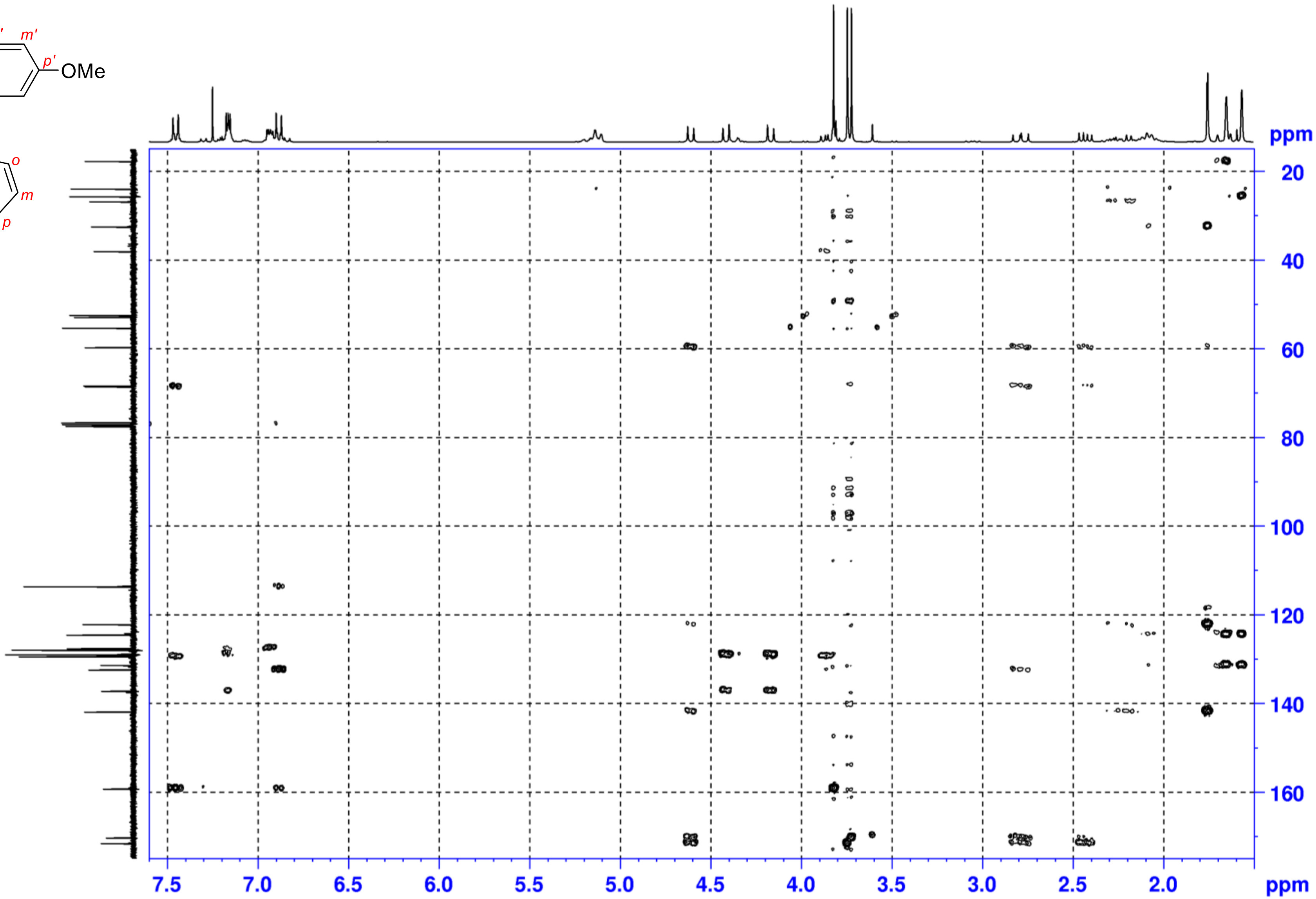

[1]H,[1]H-NOESY NMR spectrum of *Z*-**10a**, *cis*/*trans* 7.7:1 (300.1 MHz, $CDCl_3$)



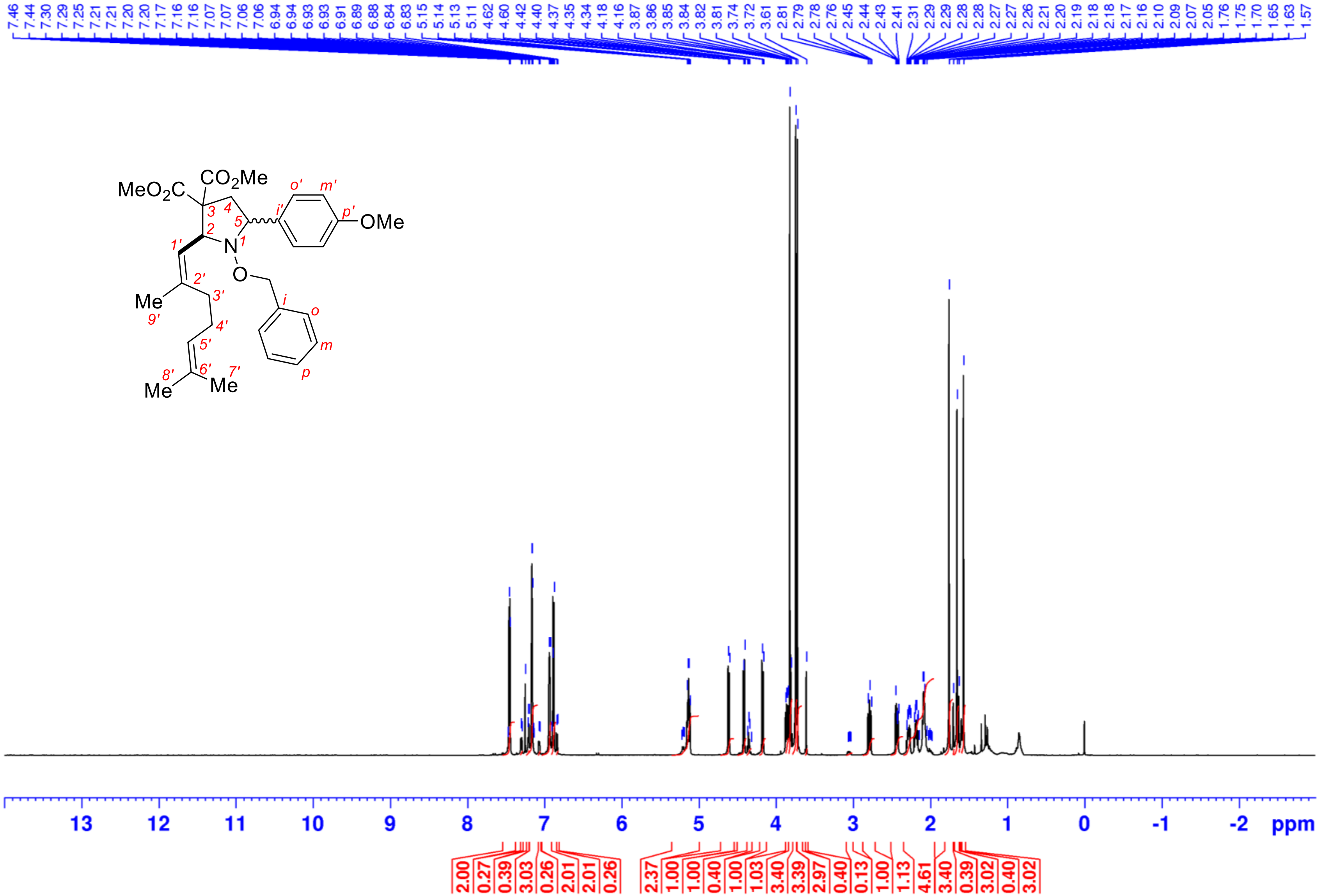


$^1H,^{13}C$-edited-HSQC NMR spectrum of *Z*-**10a**, *cis*/*trans* 7.7:1 ($^1H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

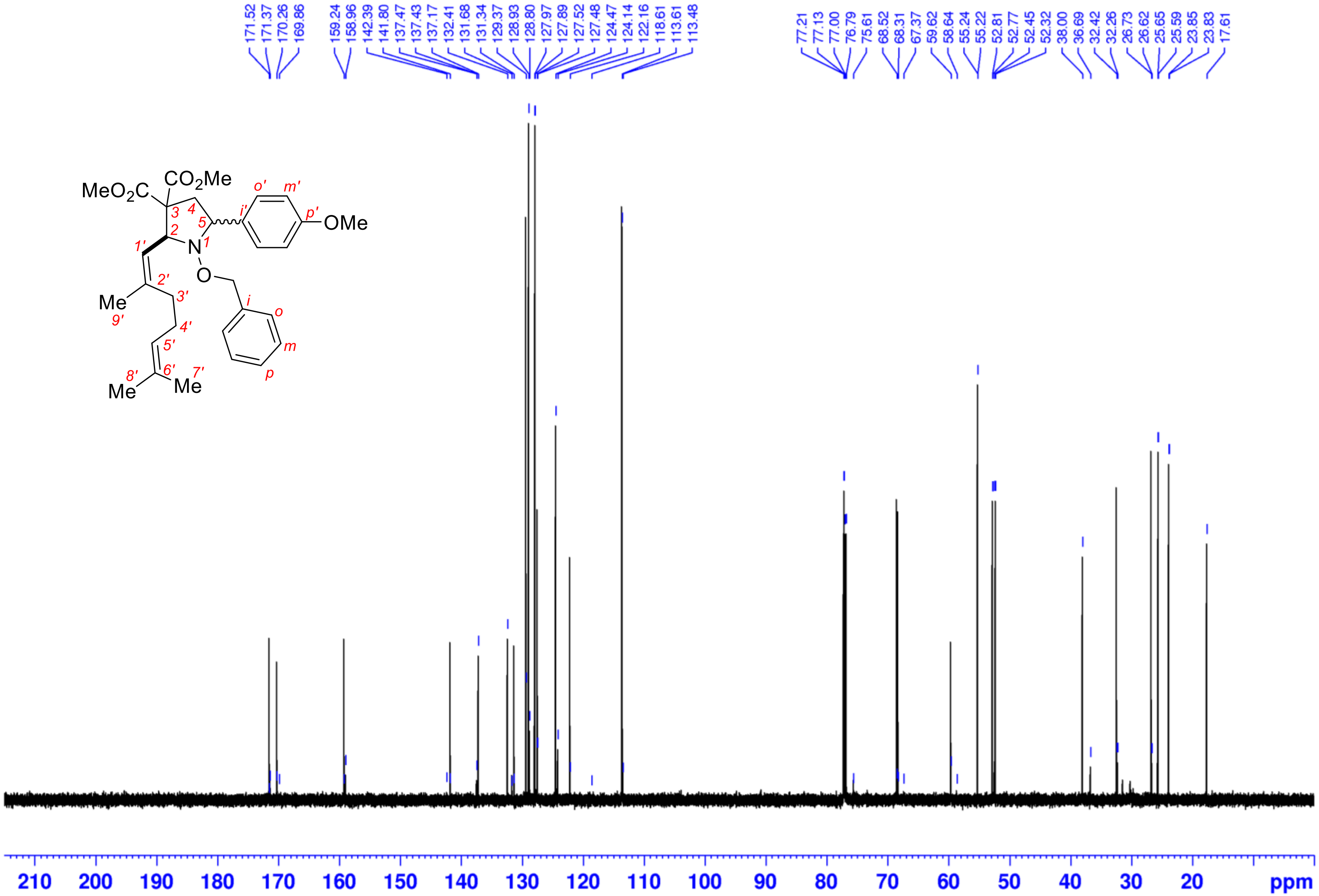




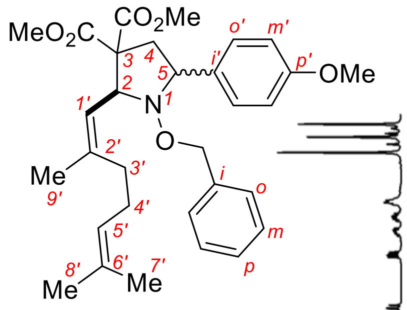

[1]H,[13]C-HMBC NMR spectrum of *Z*-**10a**, *cis*/*trans* 7.7:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

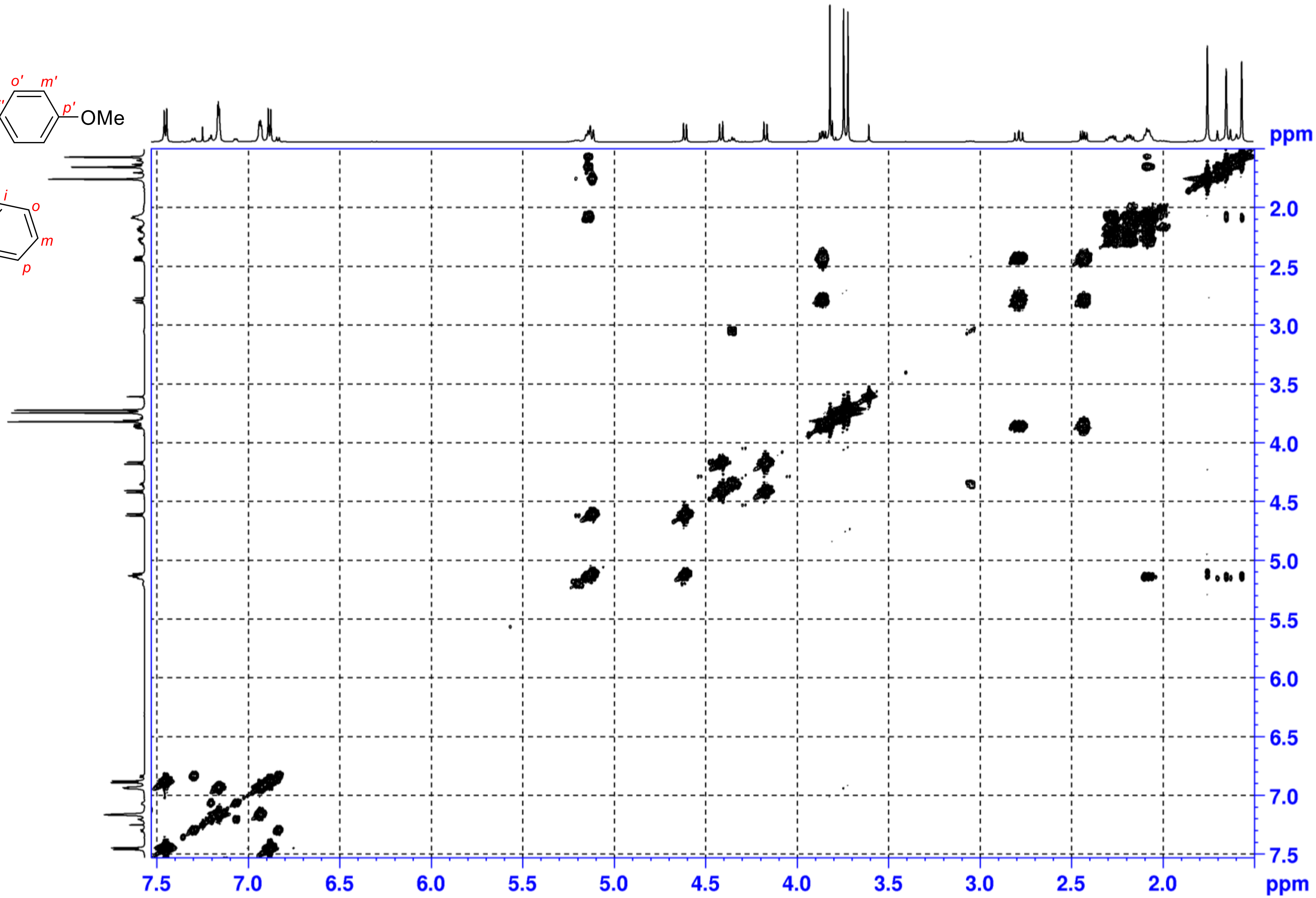



[1]H NMR spectrum of *Z*-**10a**, *cis*/*trans* 7.7:1 (600.1 MHz, $CDCl_3$)

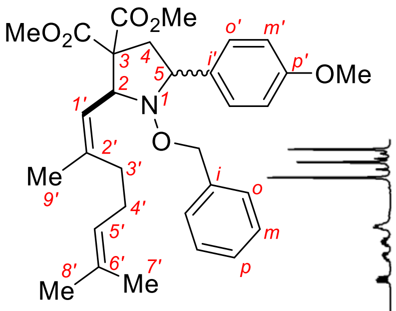


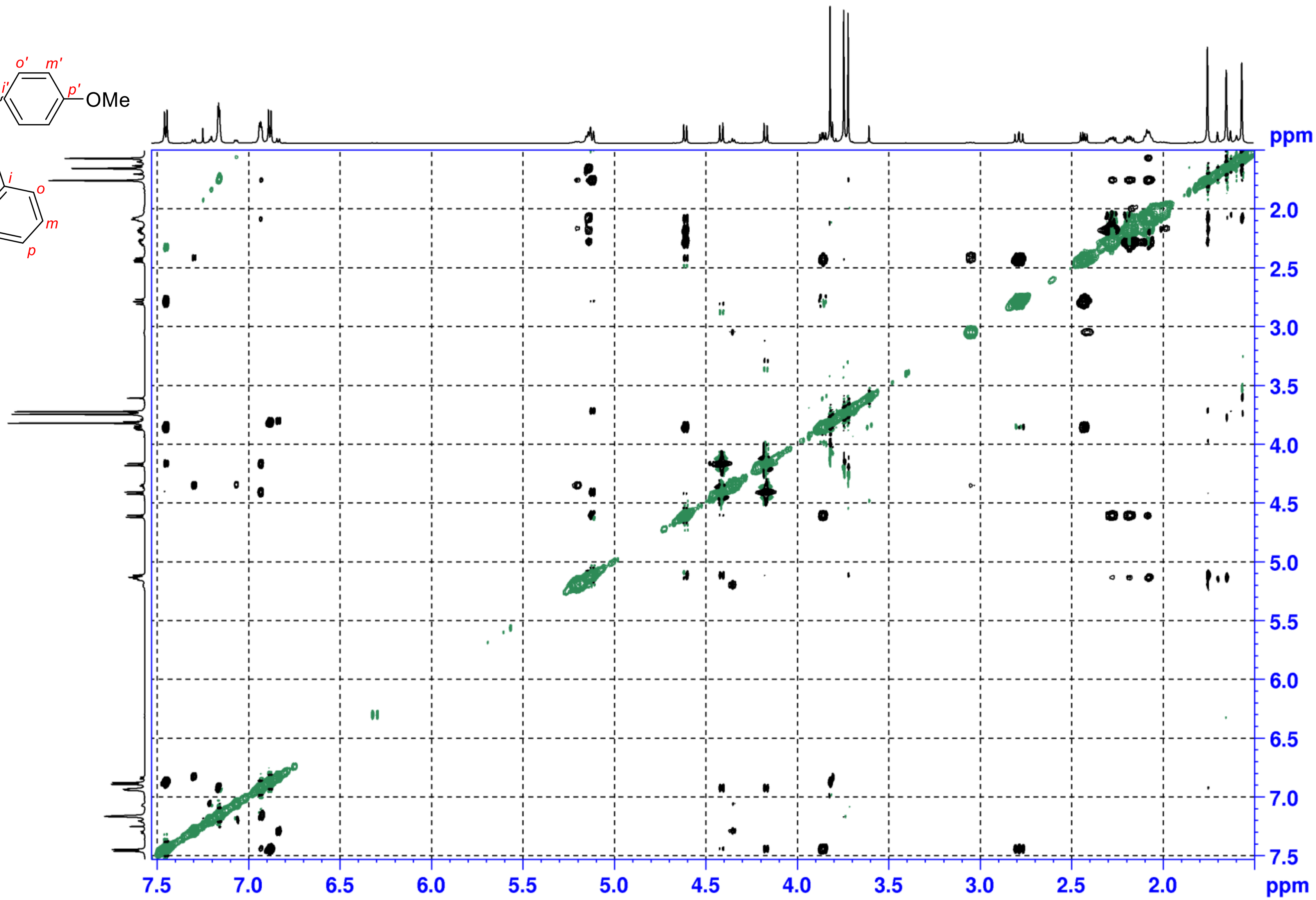

$^{13}$C NMR spectrum of *Z*-**10a**, *cis*/*trans* 7.7:1 (150.9 MHz, $CDCl_3$)



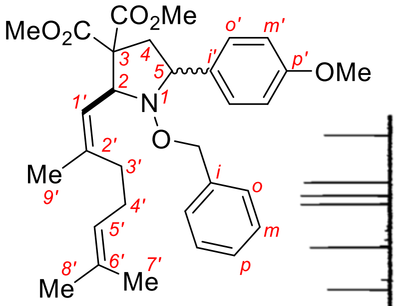



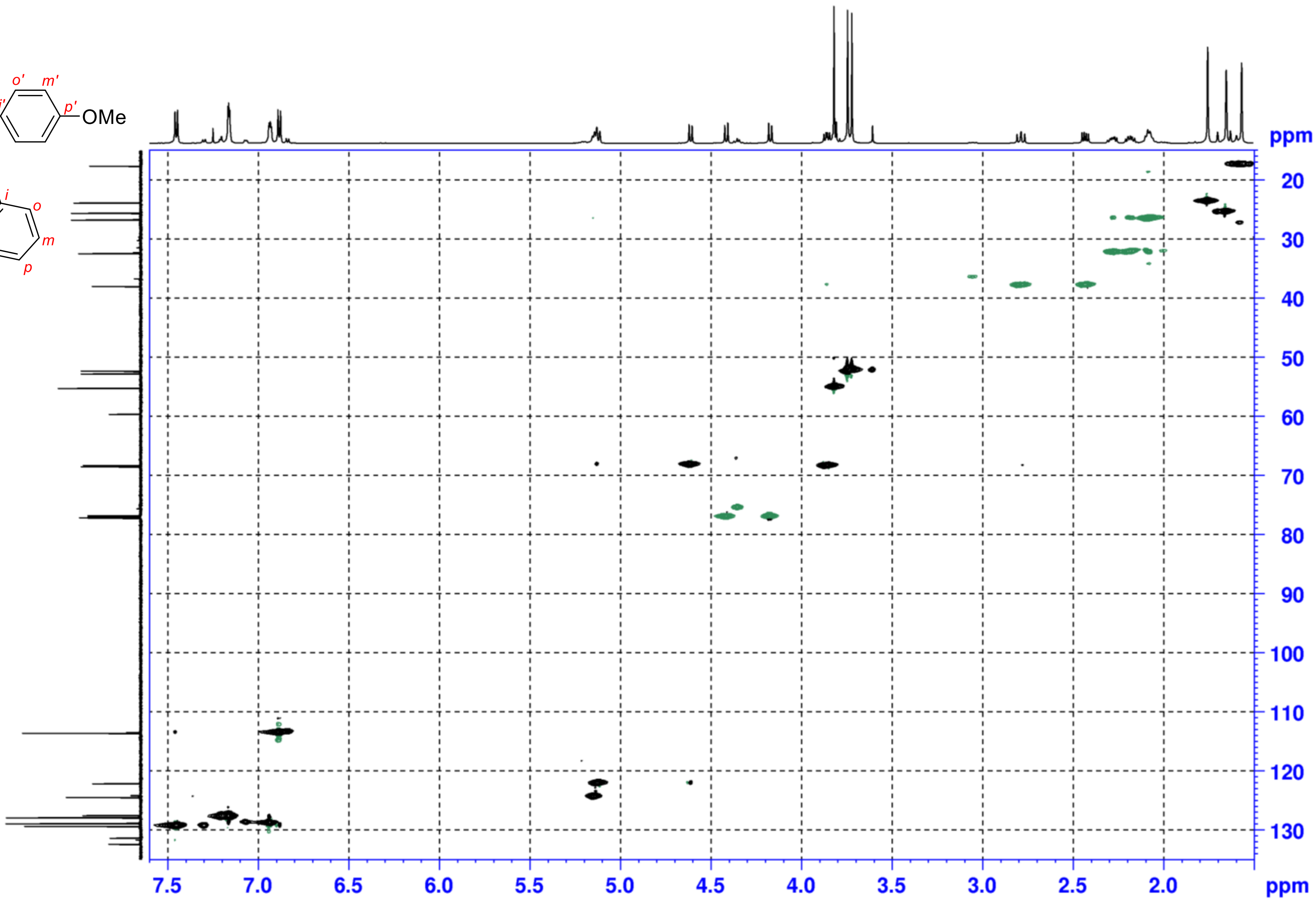

$^1H,^1H$-COSY NMR spectrum of *Z*-**10a**, *cis*/*trans* 7.7:1 (600.1 MHz, $CDCl_3$)



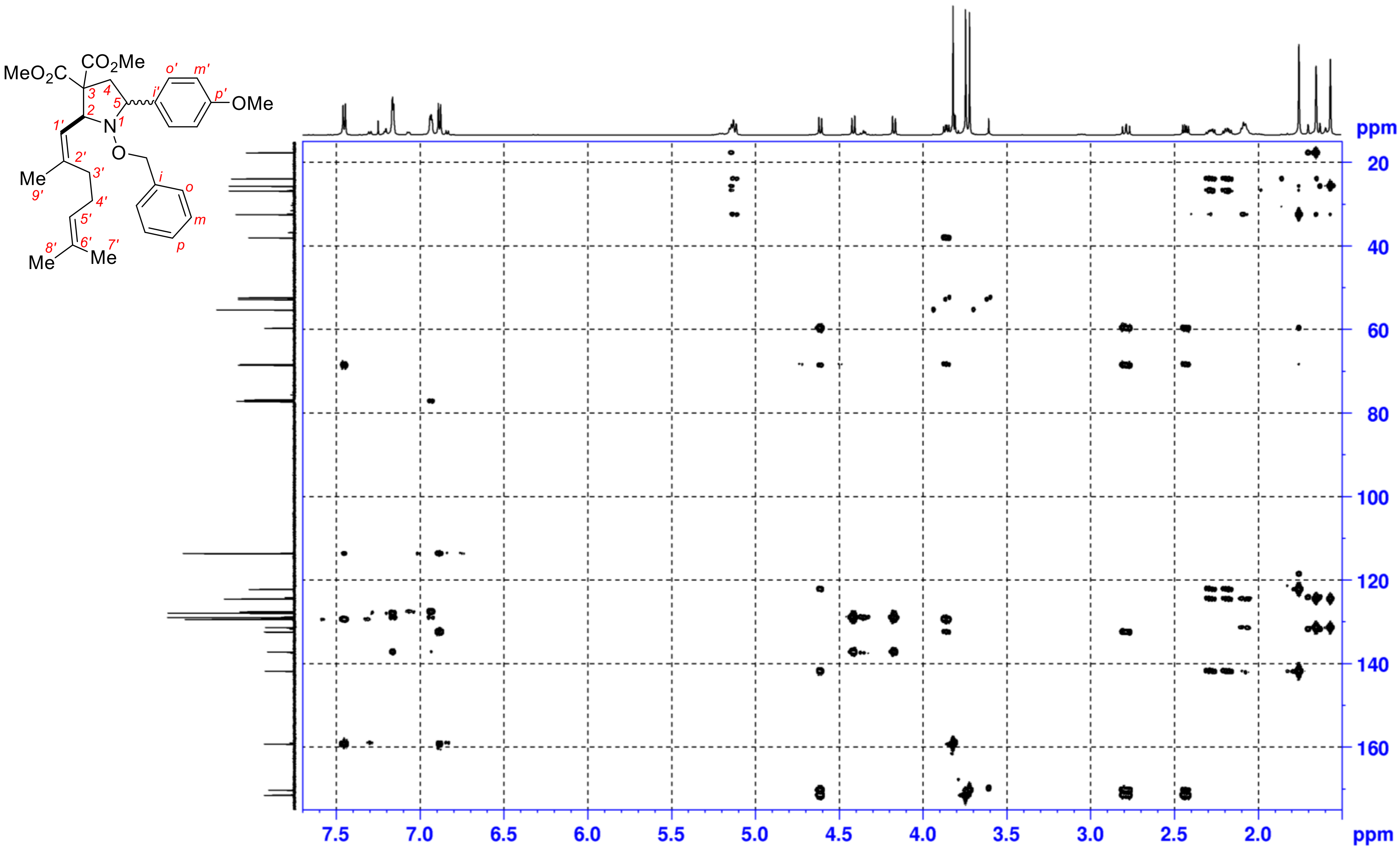


$^1H,^1H$-NOESY NMR spectrum of *Z*-**10a**, *cis*/*trans* 7.7:1 (600.1 MHz, $CDCl_3$)

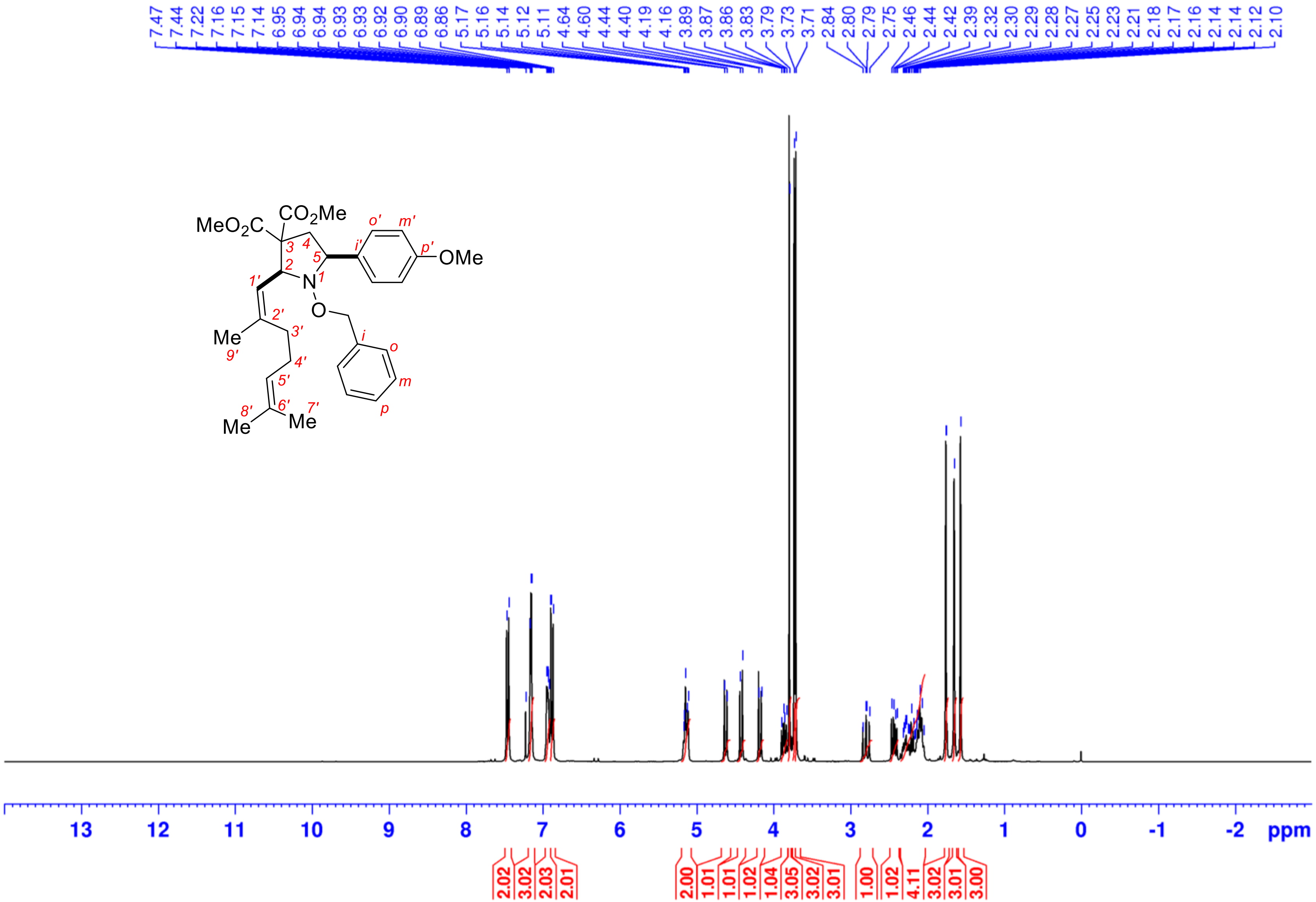


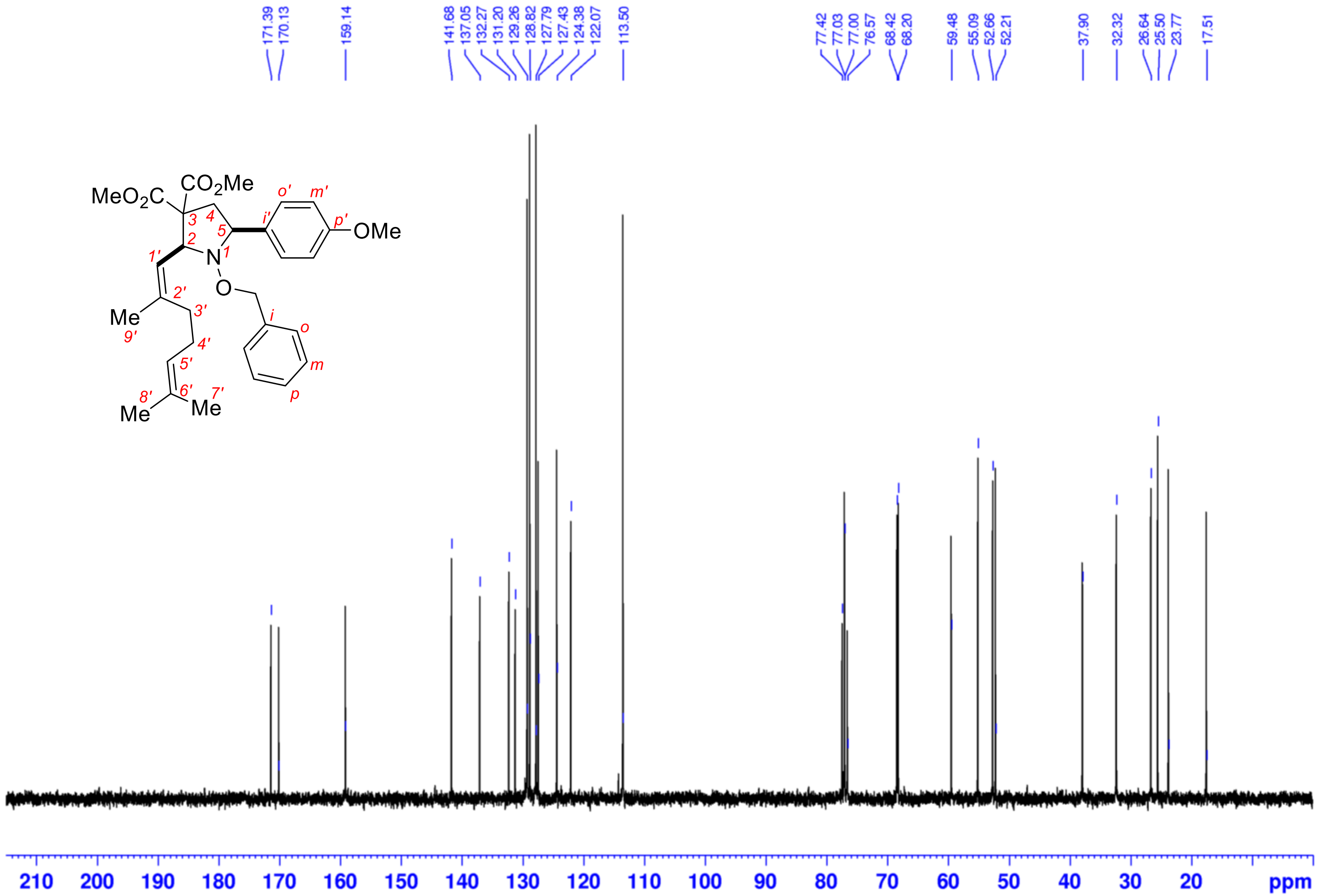

$^{1}H,^{13}C$-edited-HSQC NMR spectrum of *Z*-**10a**, *cis*/*trans* 7.7:1 ($^{1}H$: 600.1 MHz; $^{13}C$: 150.9 MHz; $CDCl_3$)



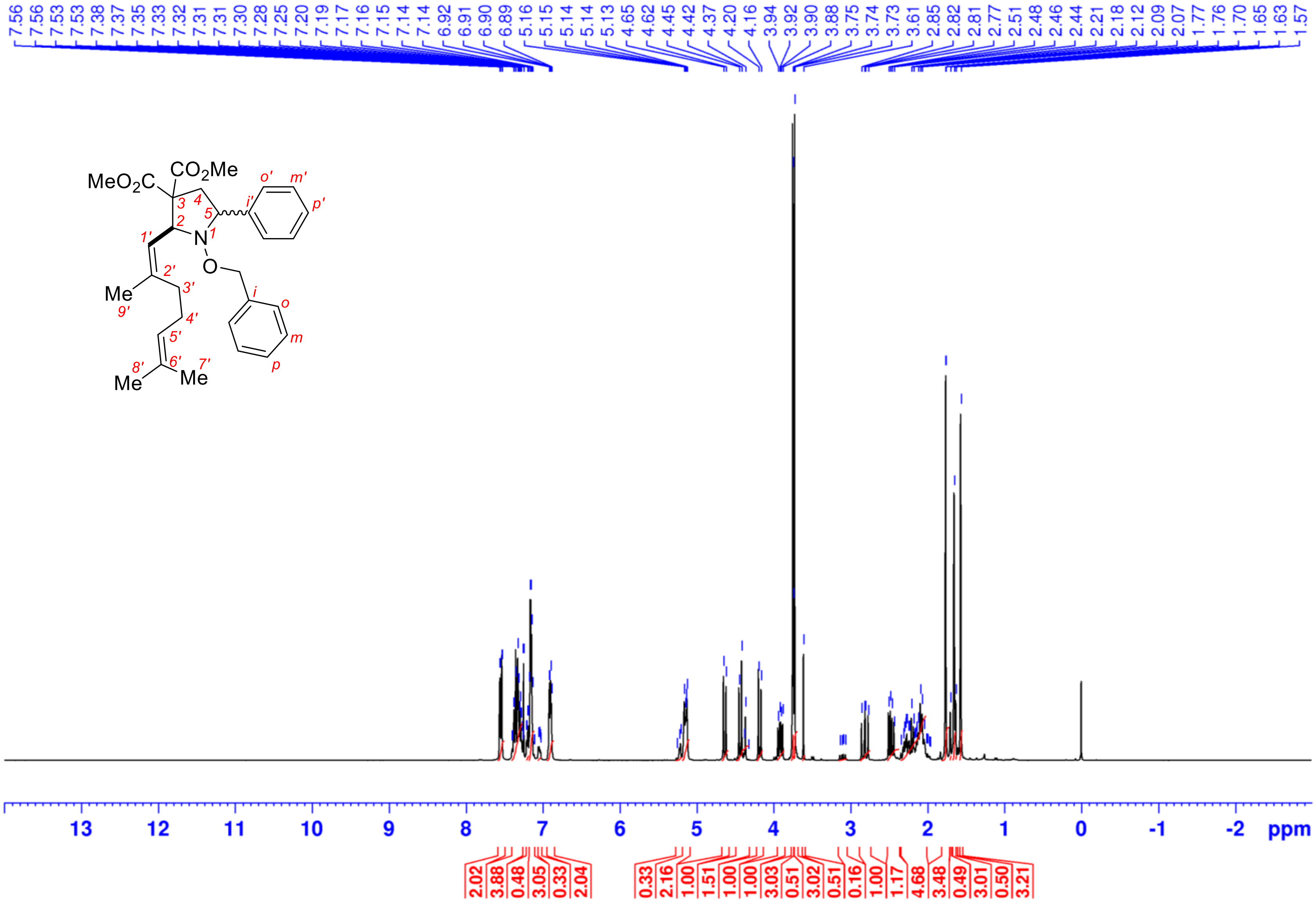
[1]H,[13]C-HMBC NMR spectrum of *Z*-**10a**, *cis*/*trans* 7.7:1 ([1]H: 600.1 MHz; [13]C: 150.9 MHz; $CDCl_3$)



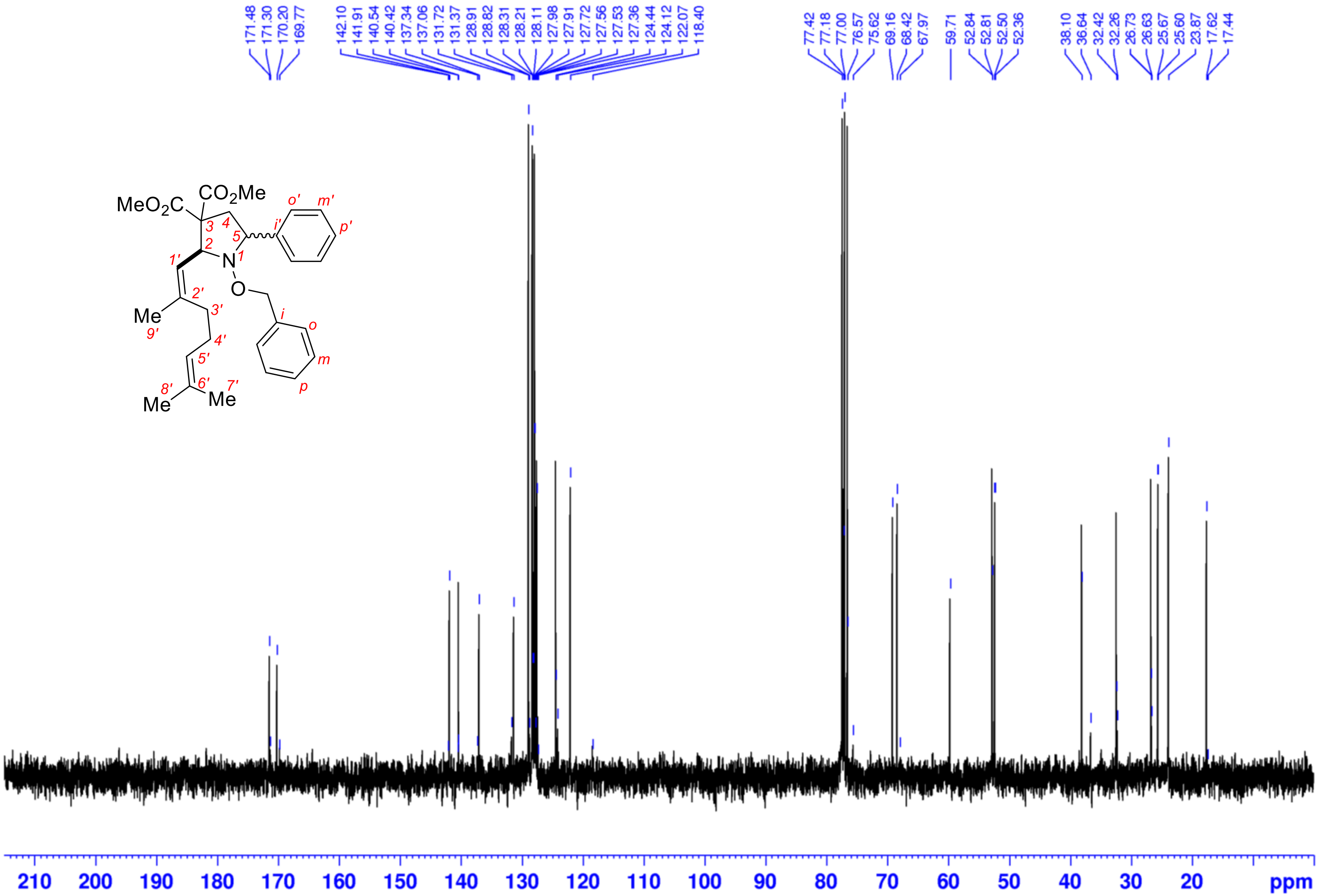
[1]H NMR spectrum of *Z,cis*-**10a** (300.1 MHz, $CDCl_3$)



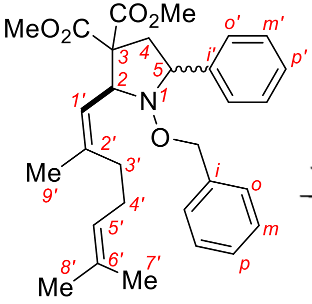

$^{13}$C NMR spectrum of *Z,cis*-**10a** (75.5 MHz, $CDCl_3$)

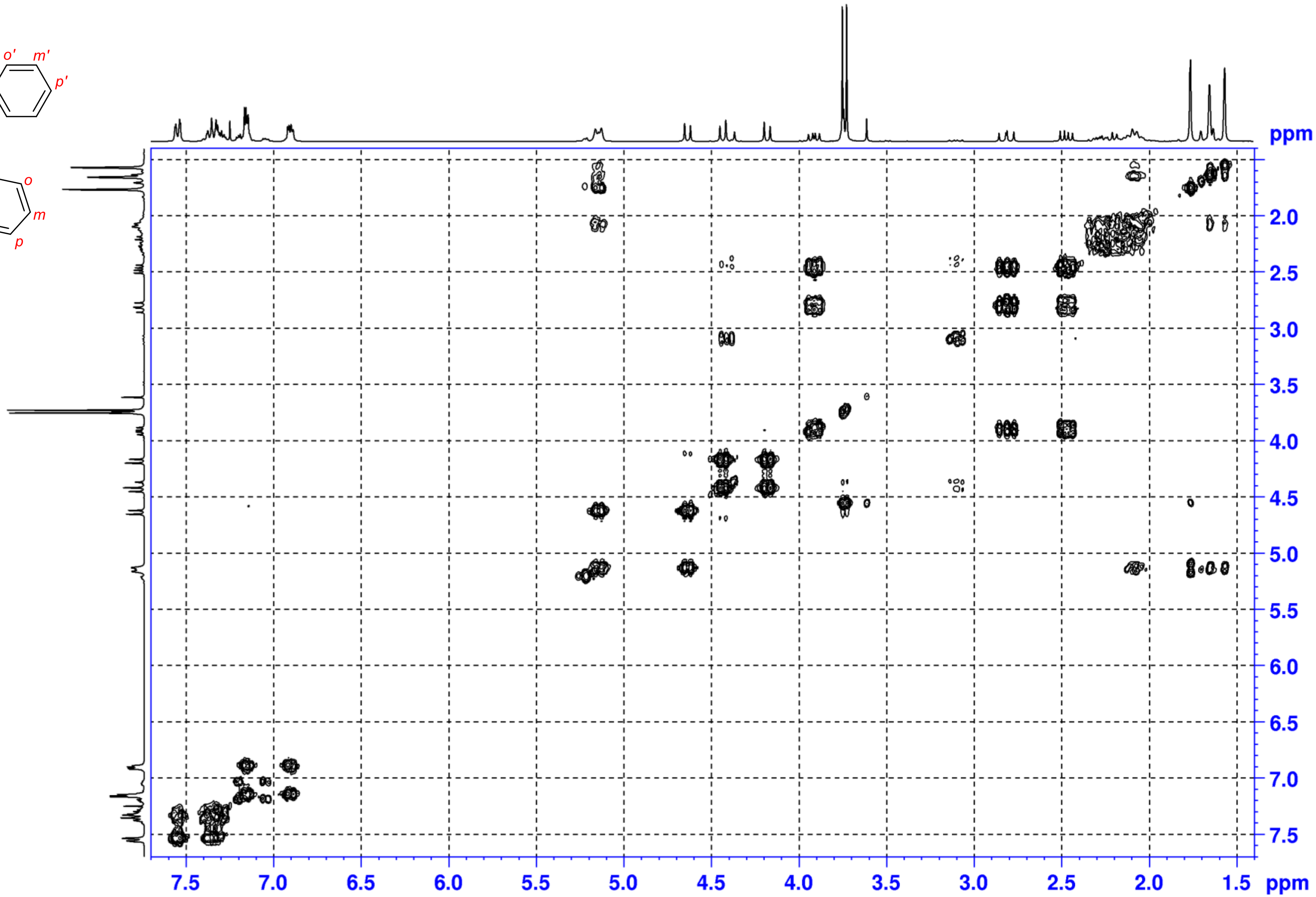


[1]H NMR spectrum of *Z*-**10d**, *cis*/*trans* 6.2:1 (300.1 MHz, $CDCl_3$)

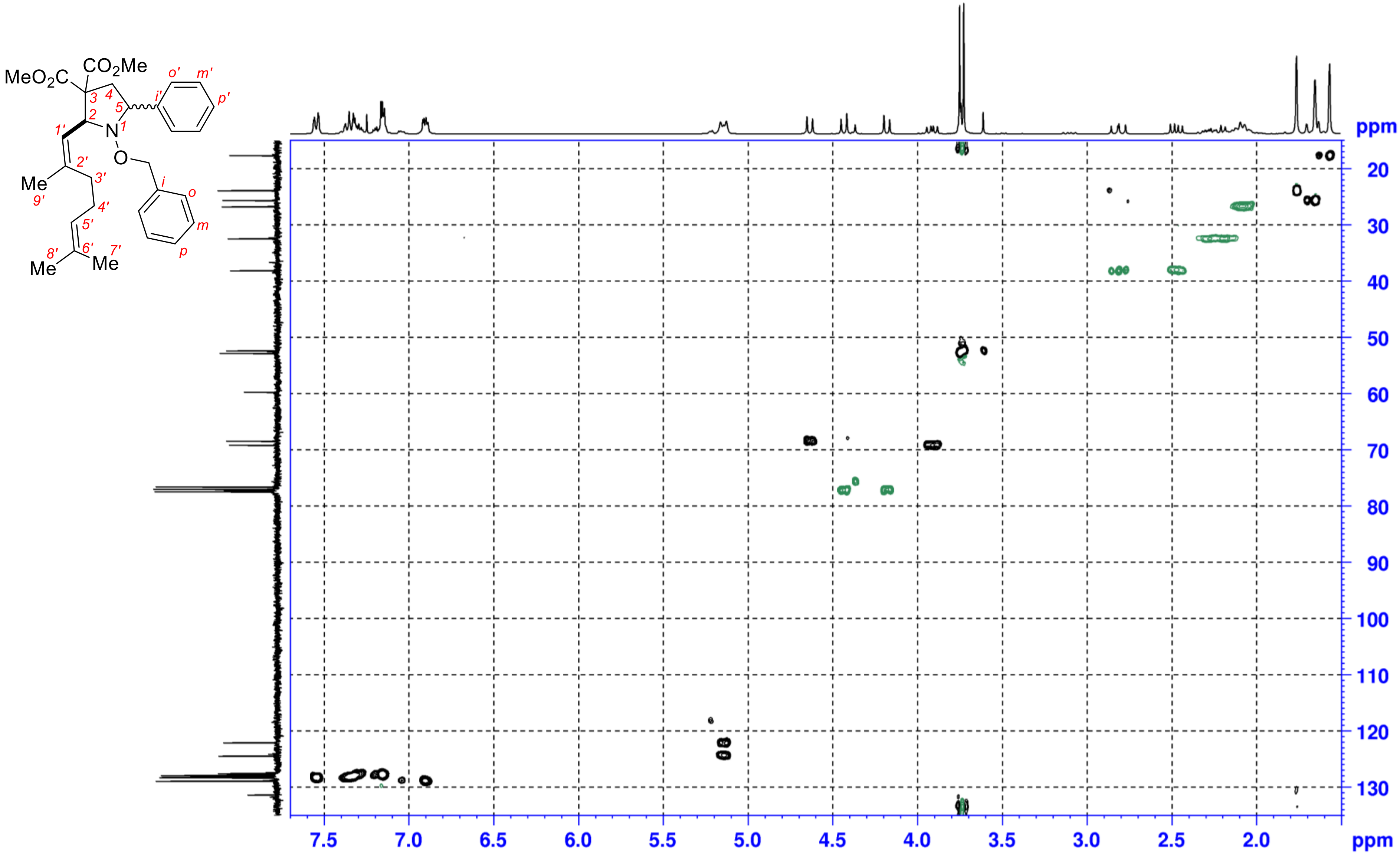



$^{13}$C NMR spectrum of *Z*-**10d**, *cis*/*trans* 6.2:1 (75.5 MHz, $CDCl_3$)

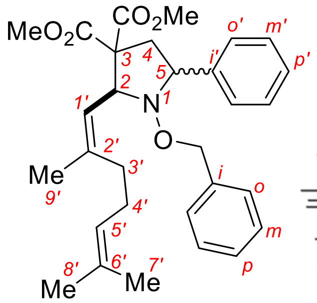


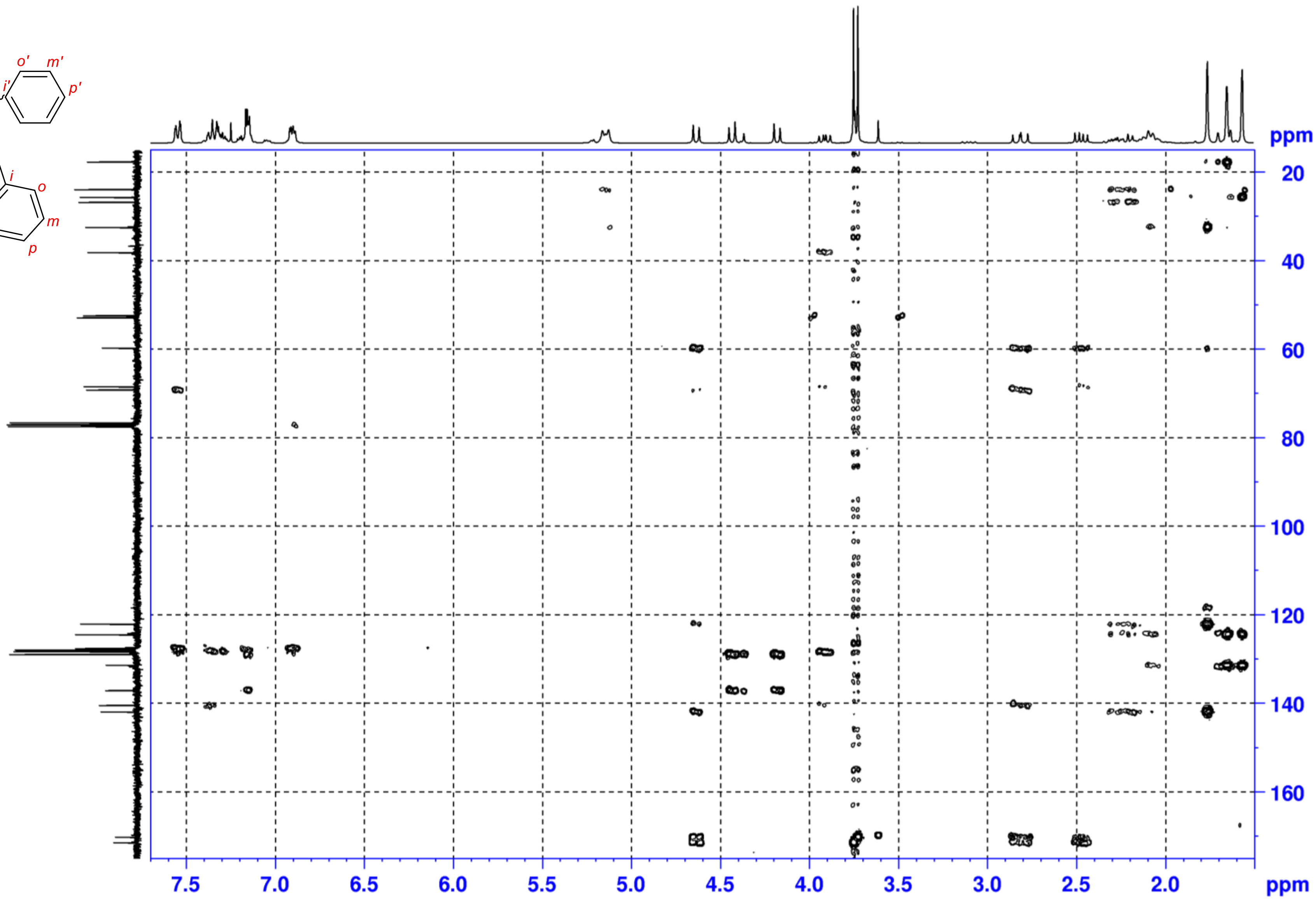




$^{1}H,^{1}H$-COSY NMR spectrum of *Z*-**10d**, *cis*/*trans* 6.2:1 (300.1 MHz, $CDCl_3$)

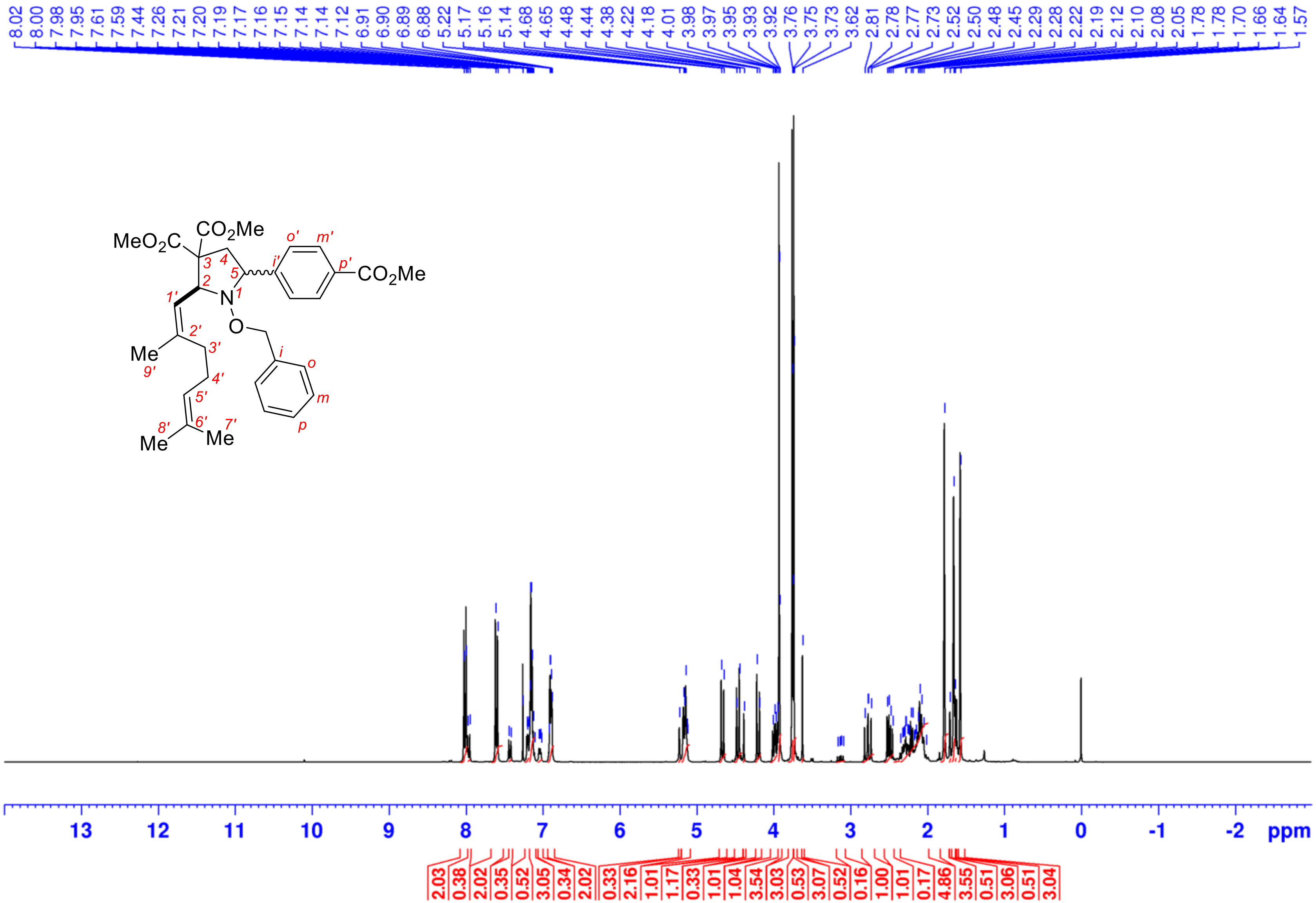


[1]H,[13]C-edited-HSQC NMR spectrum of *Z*-**10d**, *cis*/*trans* 6.2:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

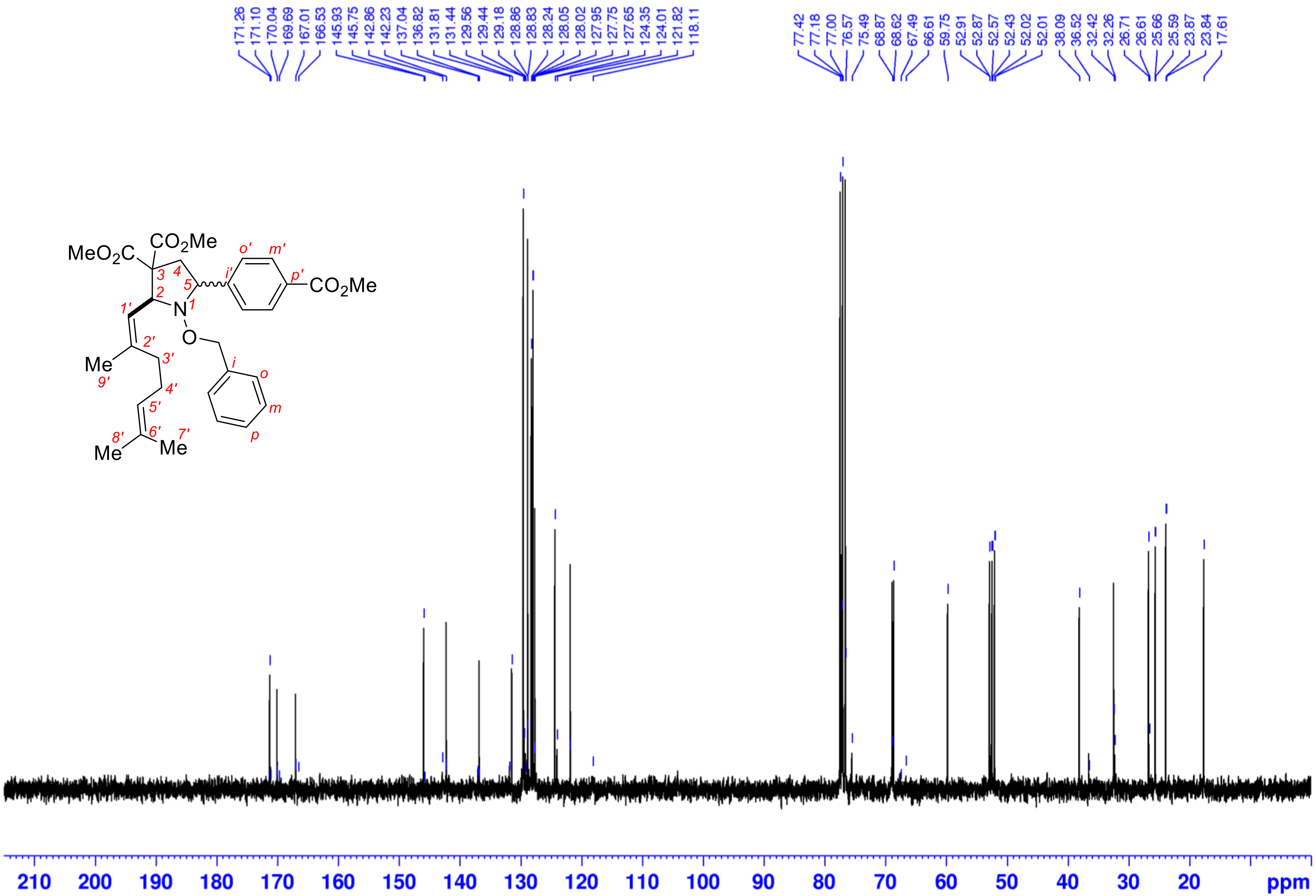


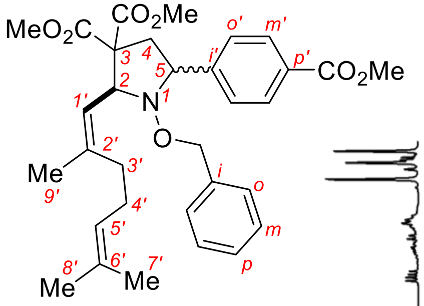

$^{1}H,^{13}C$-HMBC NMR spectrum of *Z*-**10d**, *cis*/*trans* 6.2:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

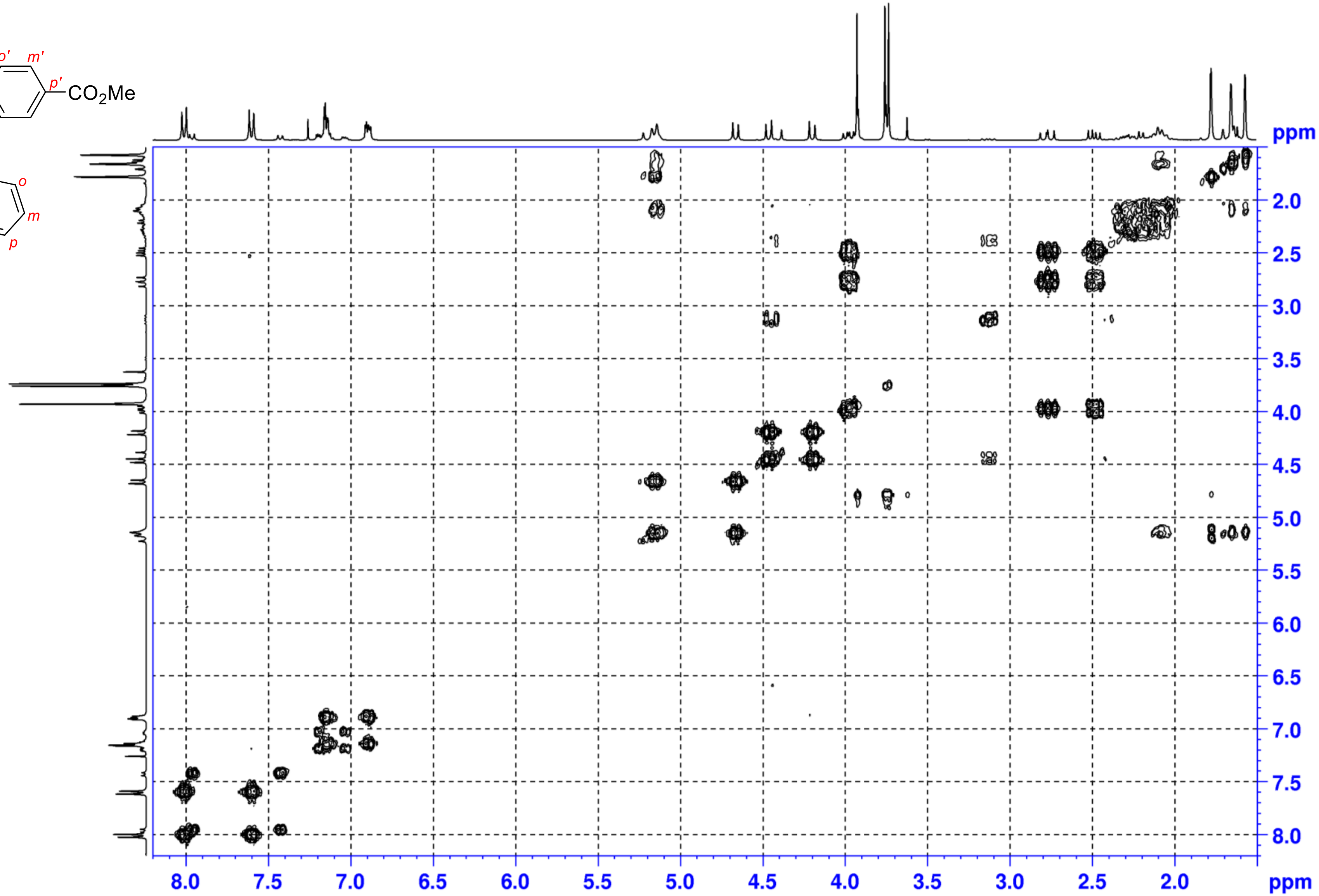


[1]H NMR spectrum of *Z*-**10k**, *cis*/*trans* 6.2:1 (300.1 MHz, $CDCl_3$)

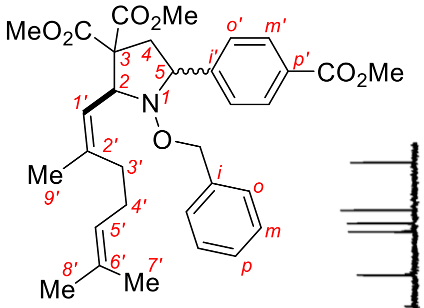


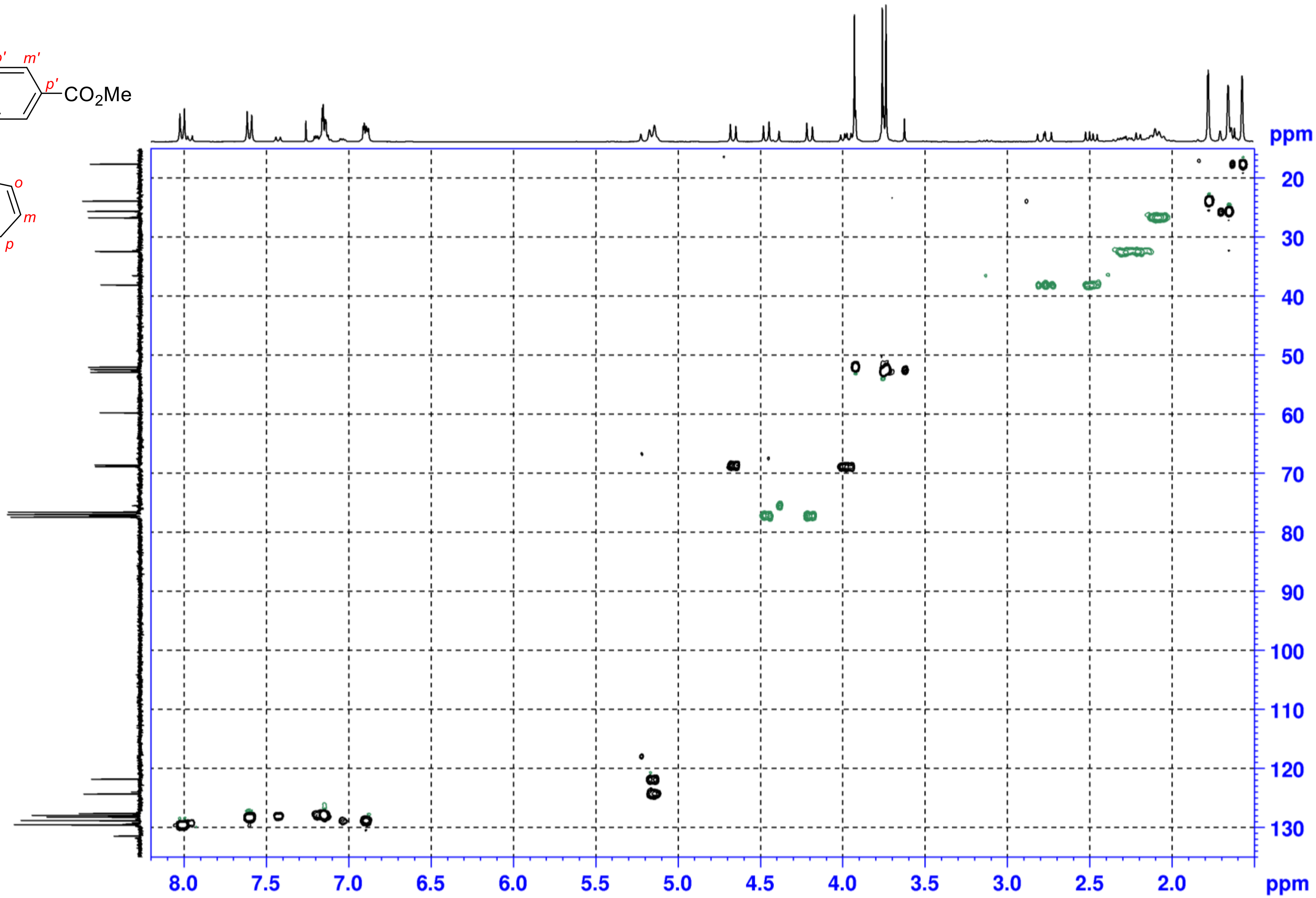

$^{13}$C NMR spectrum of *Z*-**10k**, *cis*/*trans* 6.2:1 (75.5 MHz, $CDCl_3$)



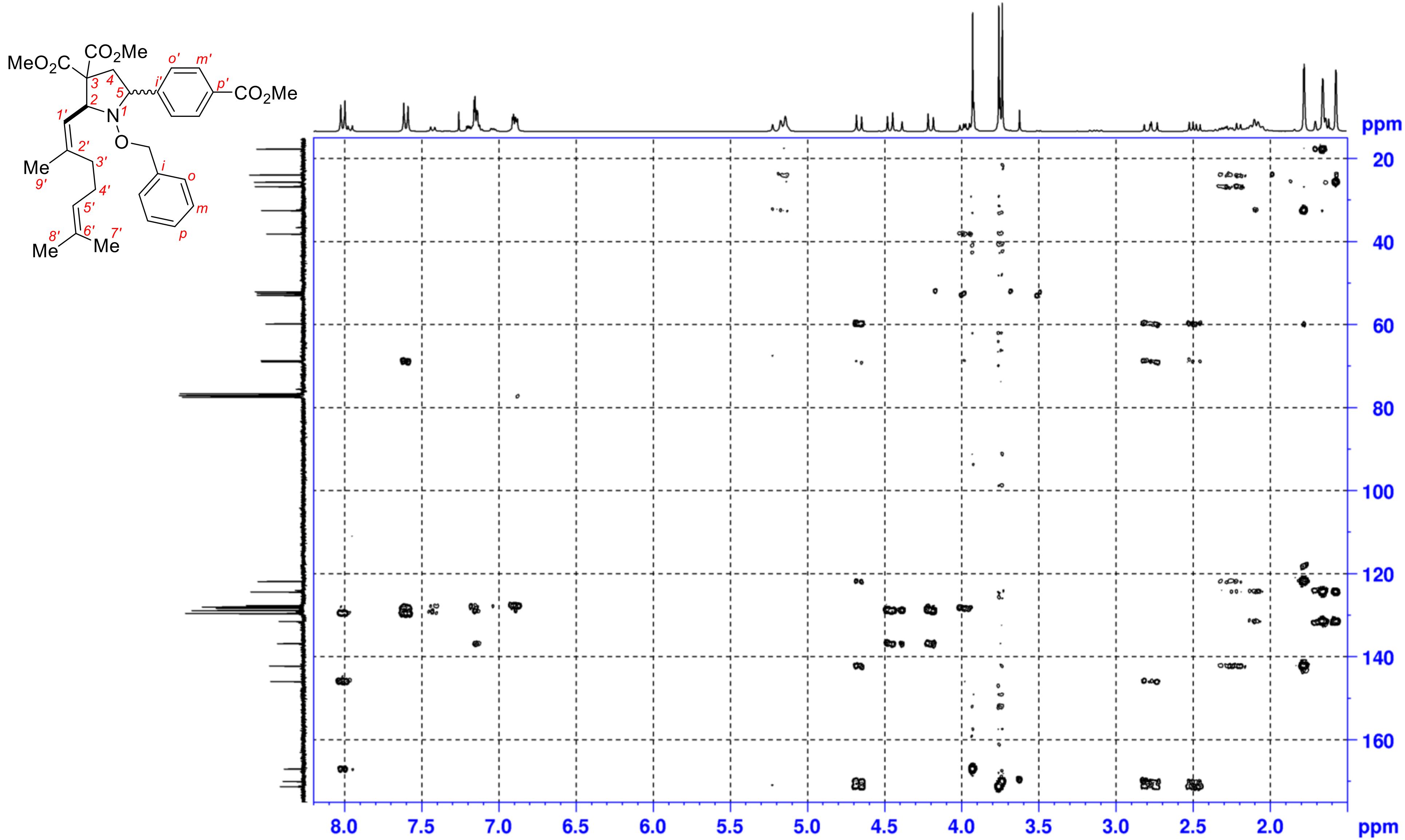




$^{1}H,^{1}H$-COSY NMR spectrum of *Z*-**10k**, *cis*/*trans* 6.2:1 (300.1 MHz, $CDCl_3$)

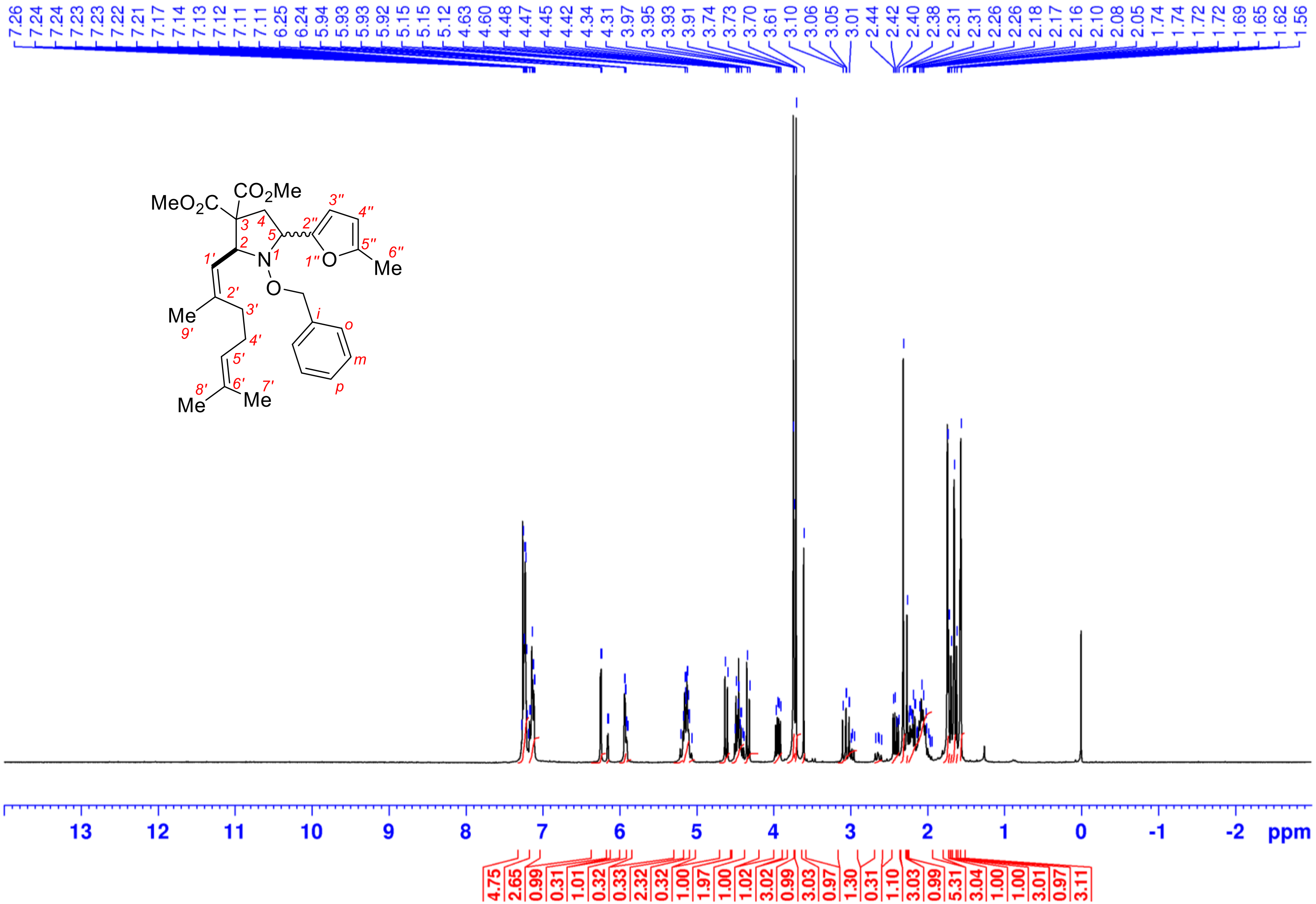




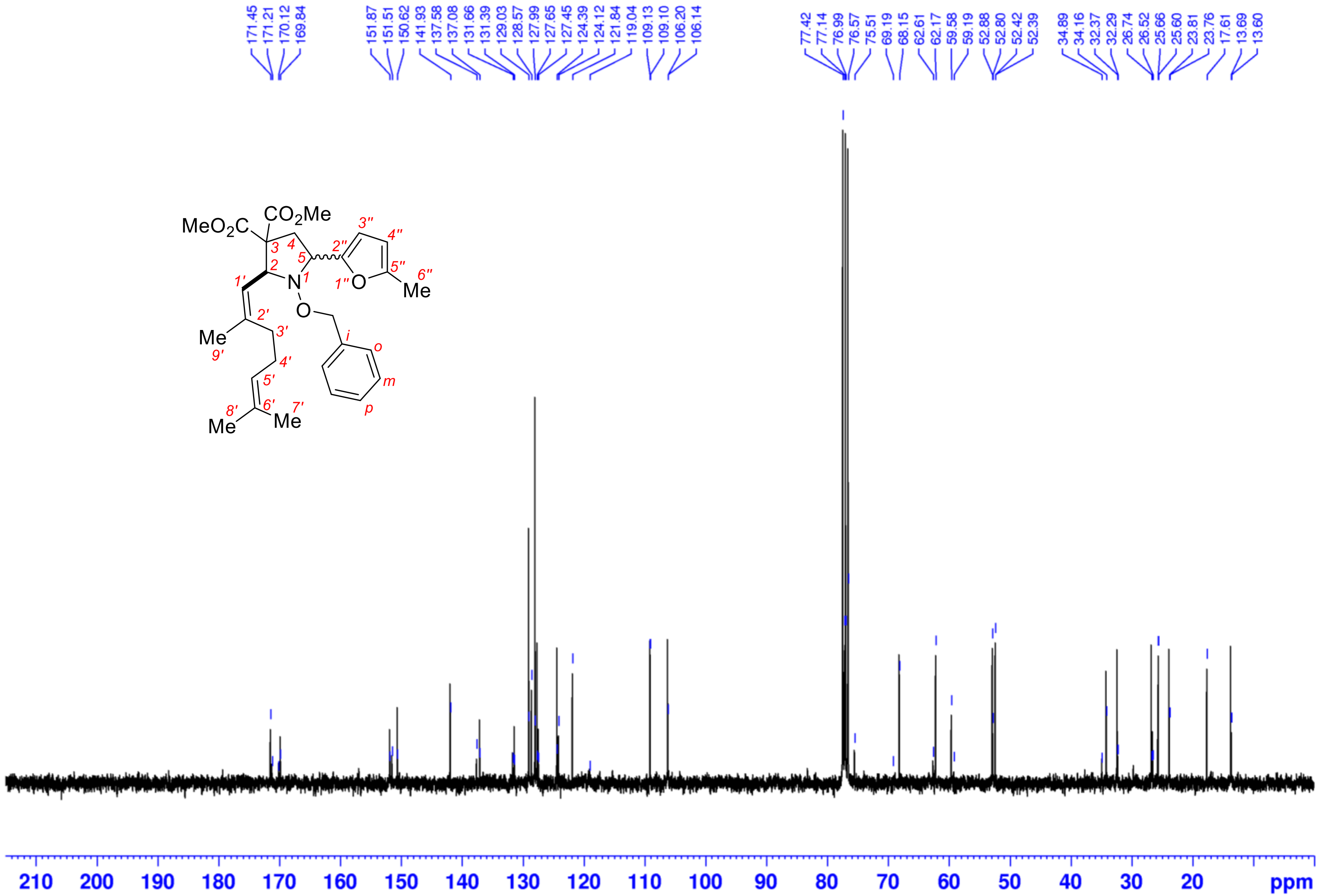

$^{1}$H,$^{13}$C-edited-HSQC NMR spectrum of *Z*-**10k**, *cis*/*trans* 6.2:1 ($^{1}$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)



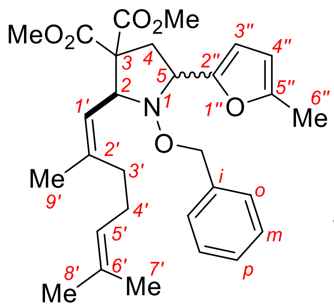

$^{1}$H,$^{13}$C-HMBC NMR spectrum of *Z*-**10k**, *cis*/*trans* 6.2:1 ($^{1}$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)

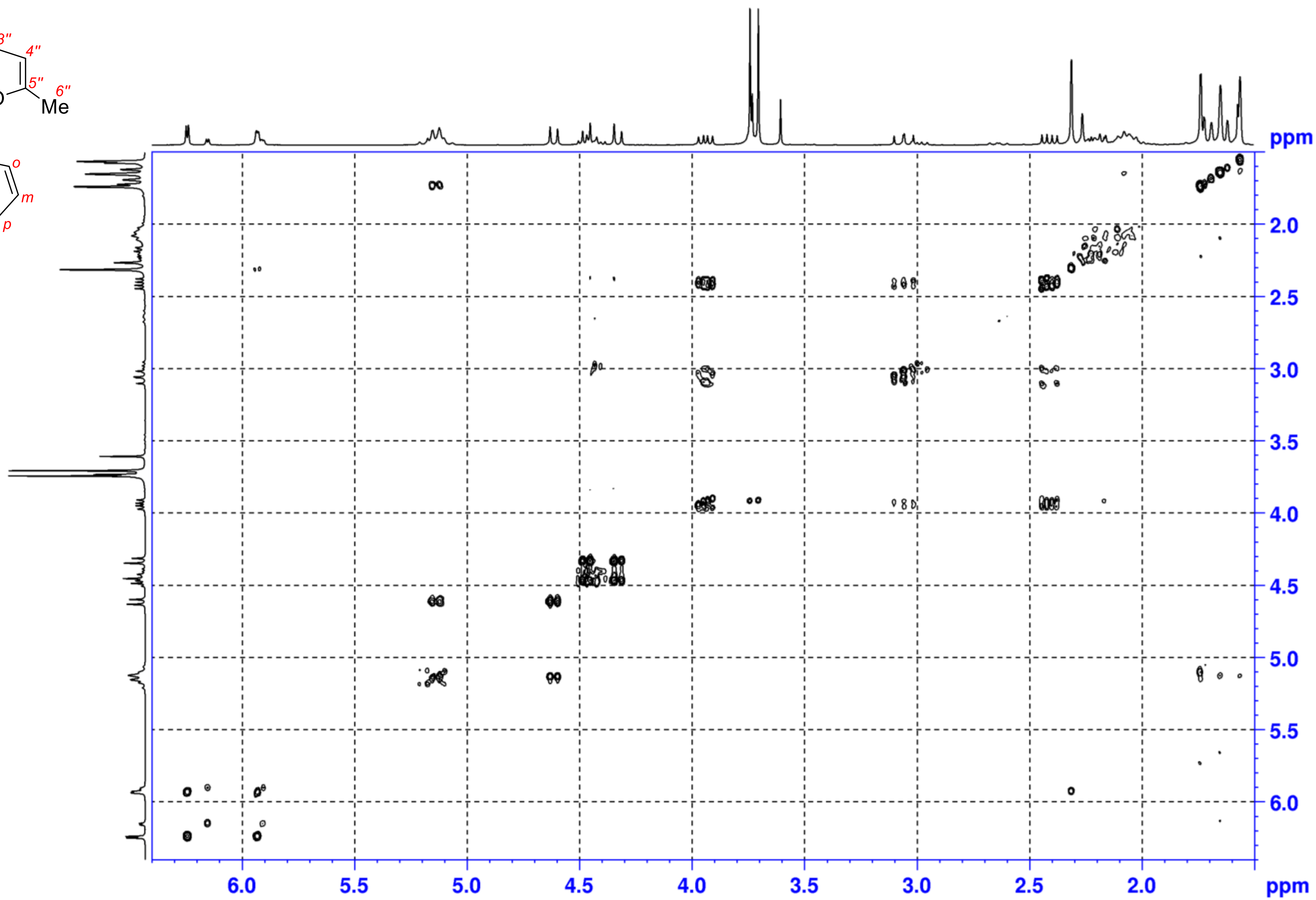


$^{1}$H NMR spectrum of *Z*-**10e**, *cis*/*trans* 3.3:1 (300.1 MHz, $CDCl_3$)

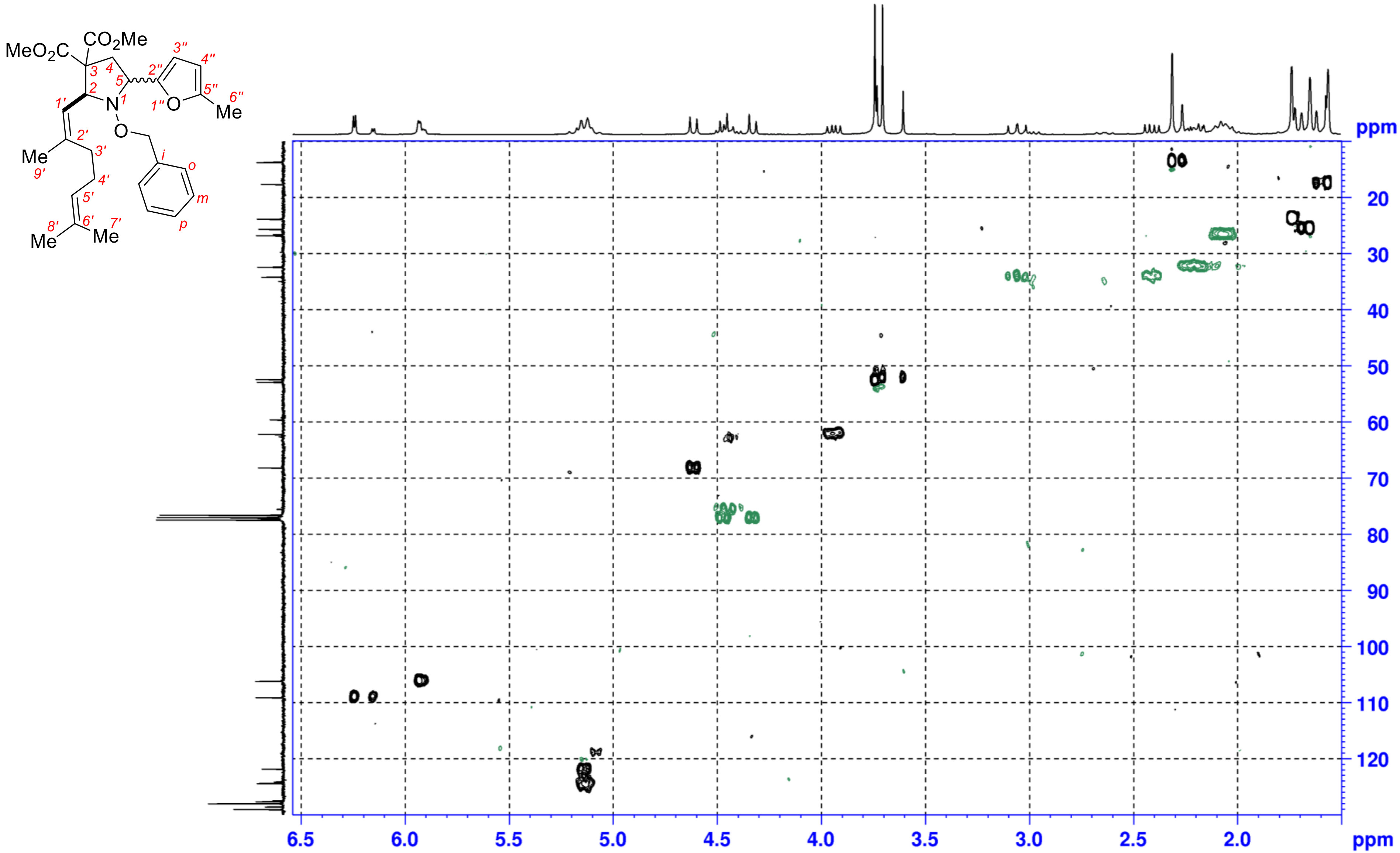



$^{13}$C NMR spectrum of *Z*-**10e**, *cis*/*trans* 3.3:1 (75.5 MHz, $CDCl_3$)

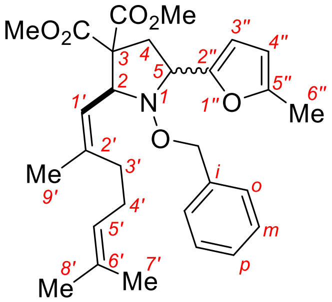


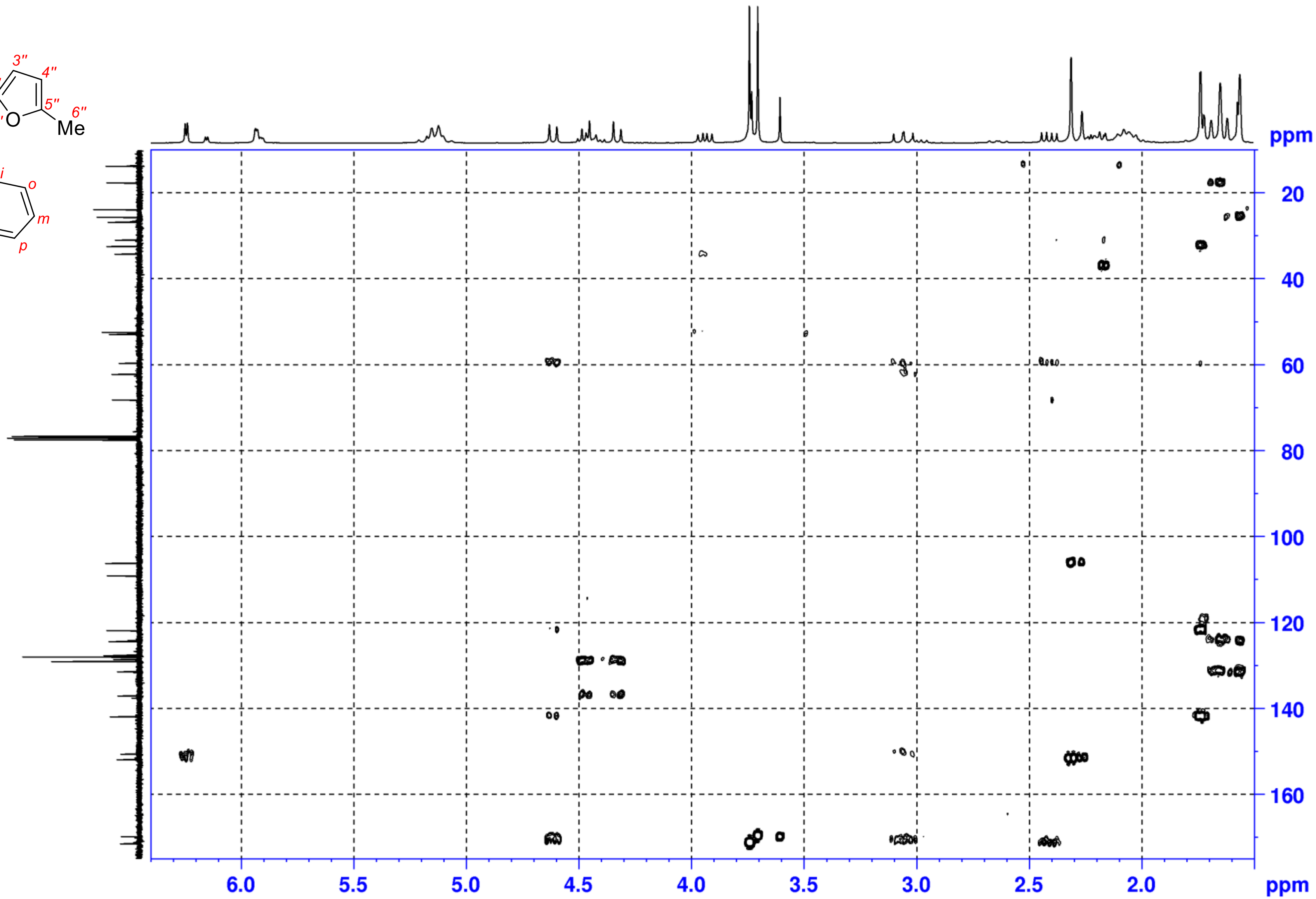




$^1H,^1H$-COSY NMR spectrum of *Z*-**10e**, *cis*/*trans* 3.3:1 (300.1 MHz, $CDCl_3$)

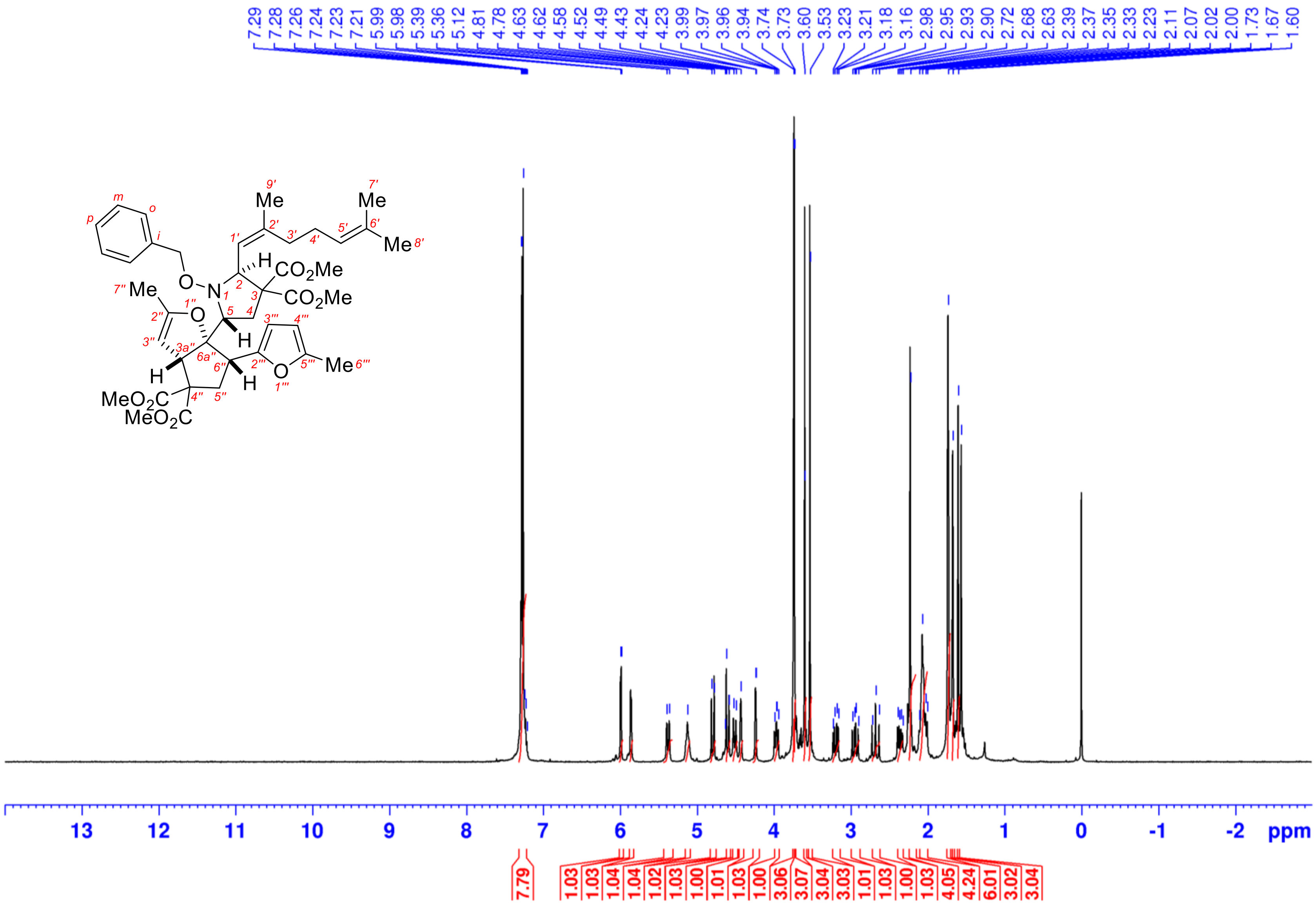



$^{1}$H,$^{13}$C-edited-HSQC NMR spectrum of *Z*-**10e**, *cis*/*trans* 3.3:1 ($^{1}$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)

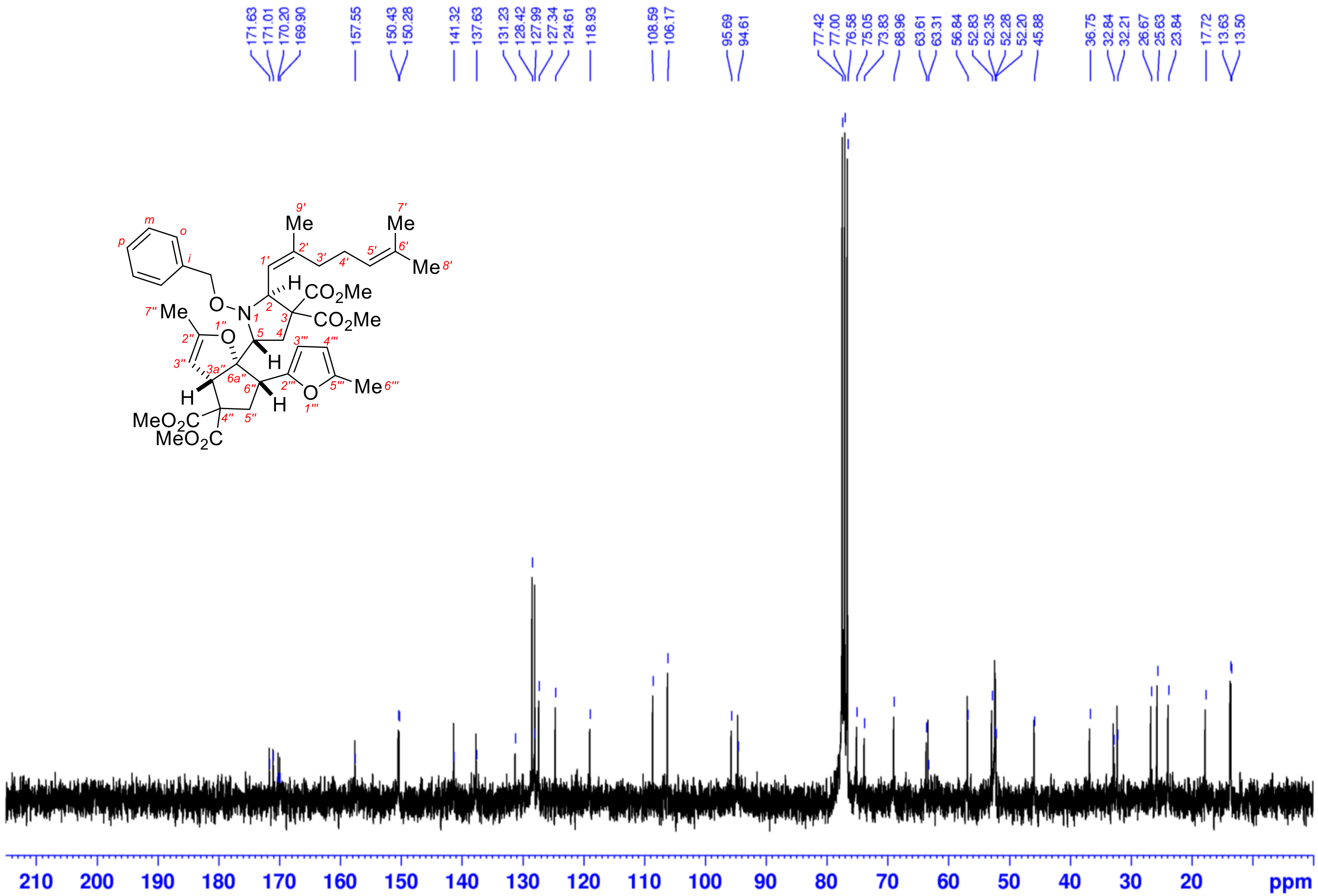


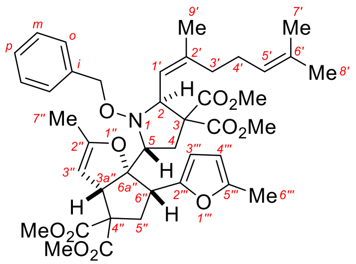

[1]H,[13]C-HMBC NMR spectrum of *Z*-**10e**, *cis*/*trans* 3.3:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

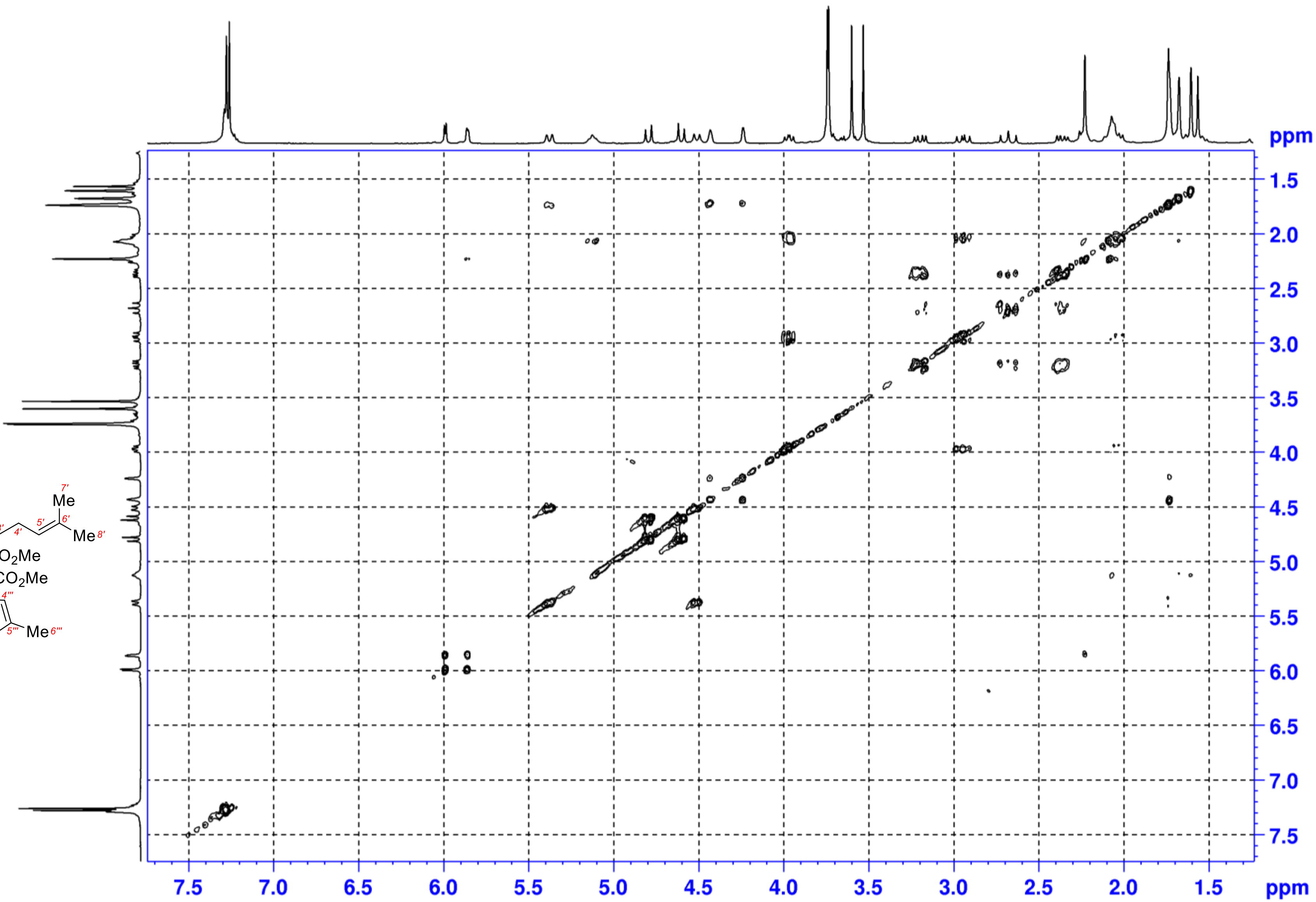


[1]H NMR spectrum of (2*RS*,5*SR*)-**11** (300.1 MHz, $CDCl_3$)

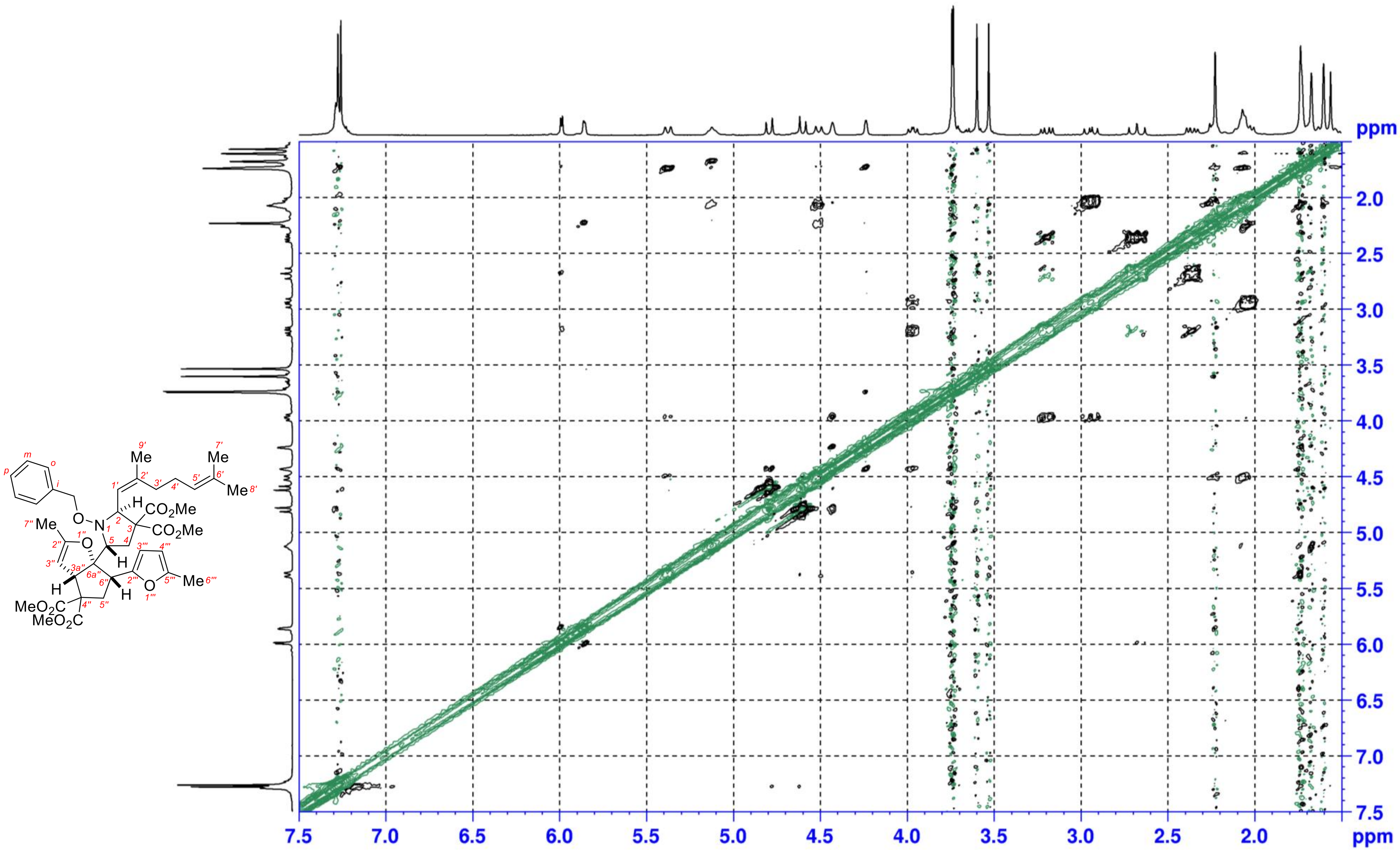



$^{13}$C NMR spectrum of (2*RS*,5*SR*)-**11** (75.5 MHz, $CDCl_3$)

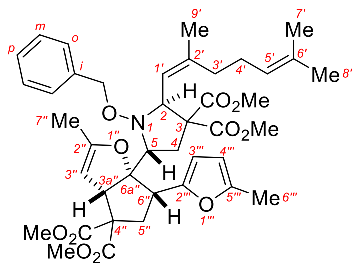


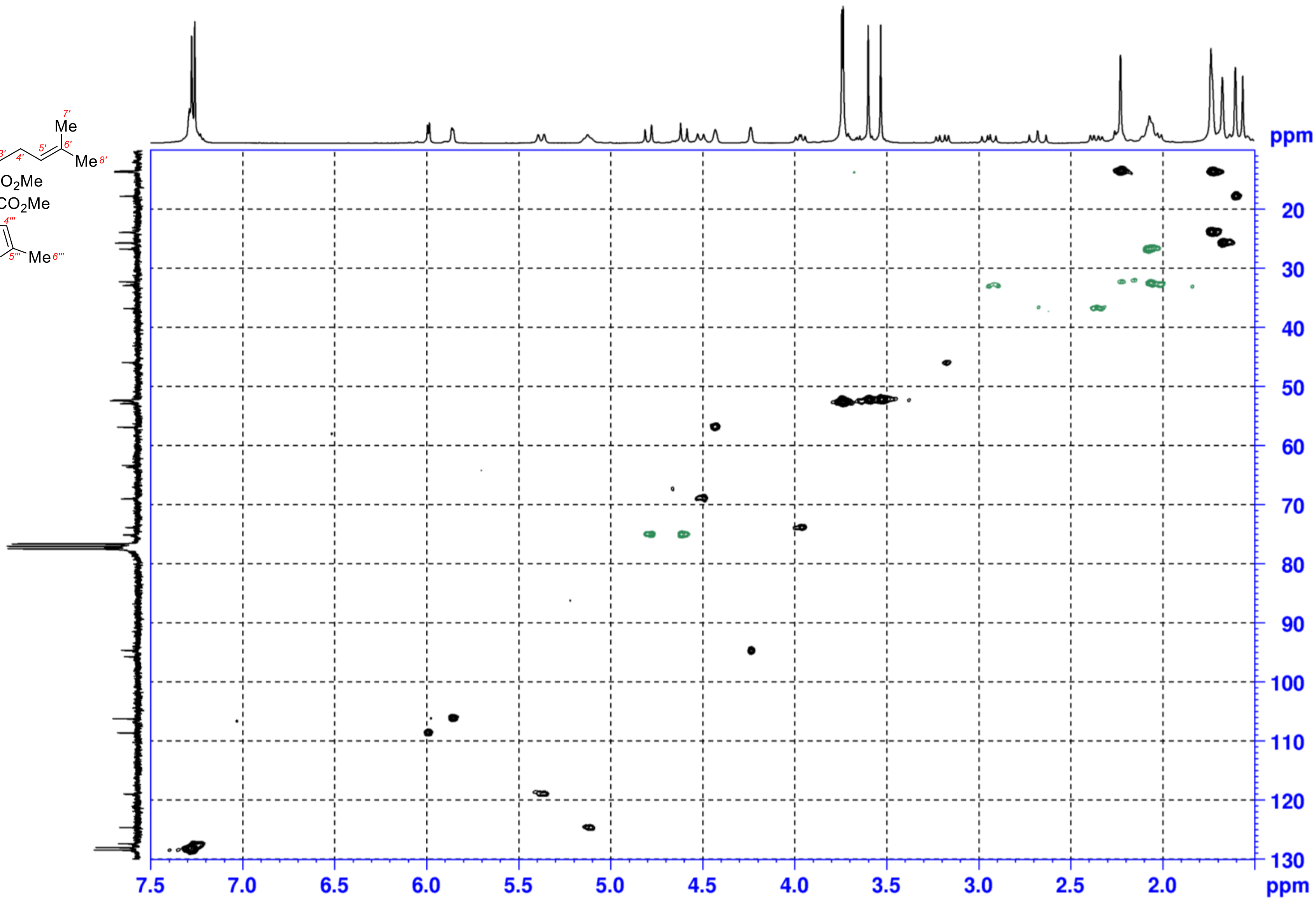



$^{1}$H,$^{1}$H-COSY NMR spectrum of (2*RS*,5*SR*)-**11** (300.1 MHz, $CDCl_3$)

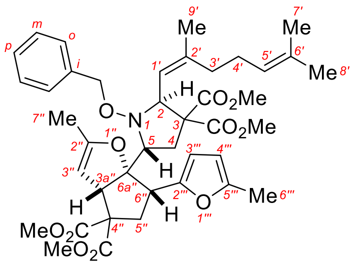
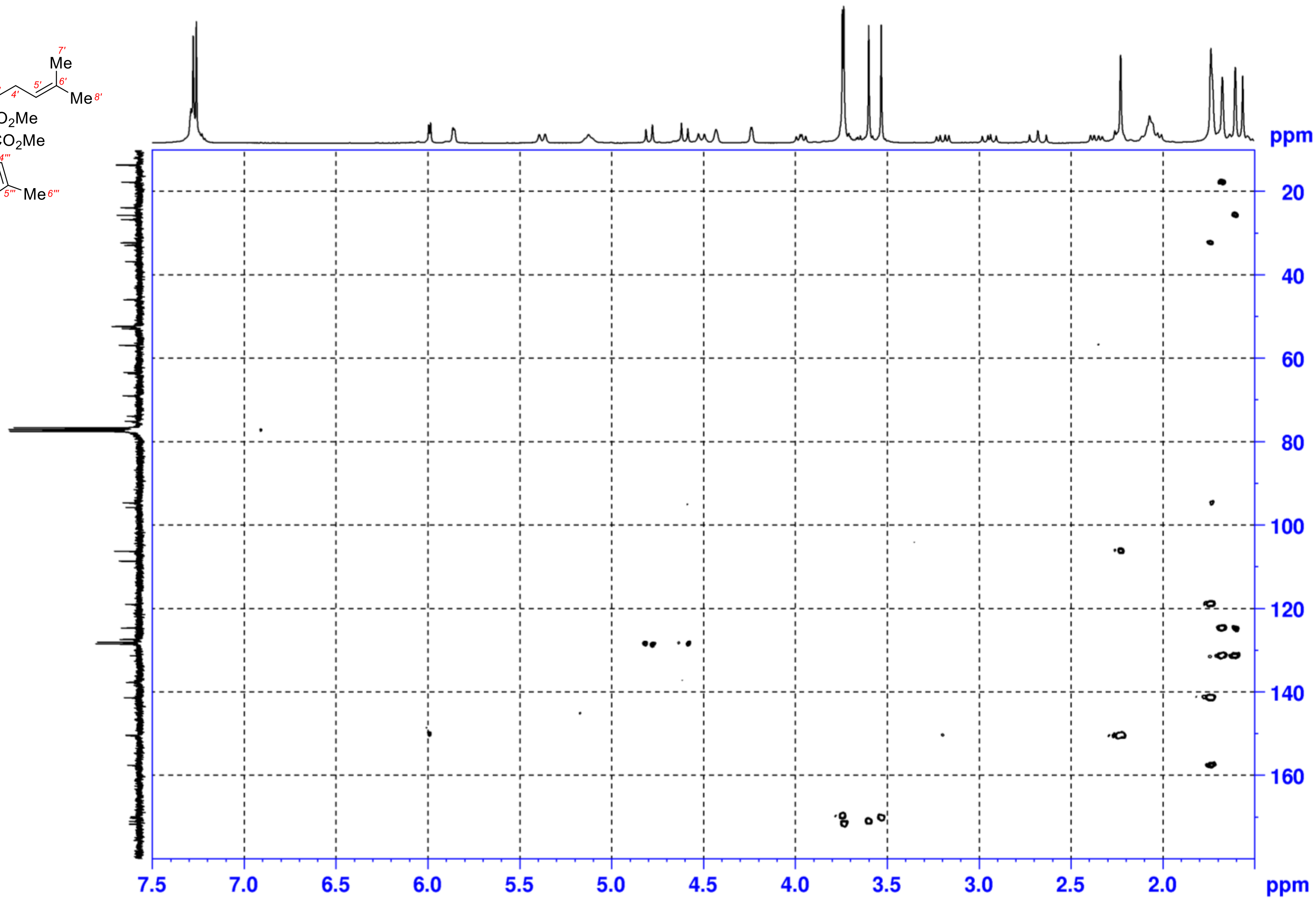



$^{1}H$,$^{1}H$-NOESY NMR spectrum of (2*RS*,5*SR*)-**11** (300.1 MHz, $CDCl_3$)

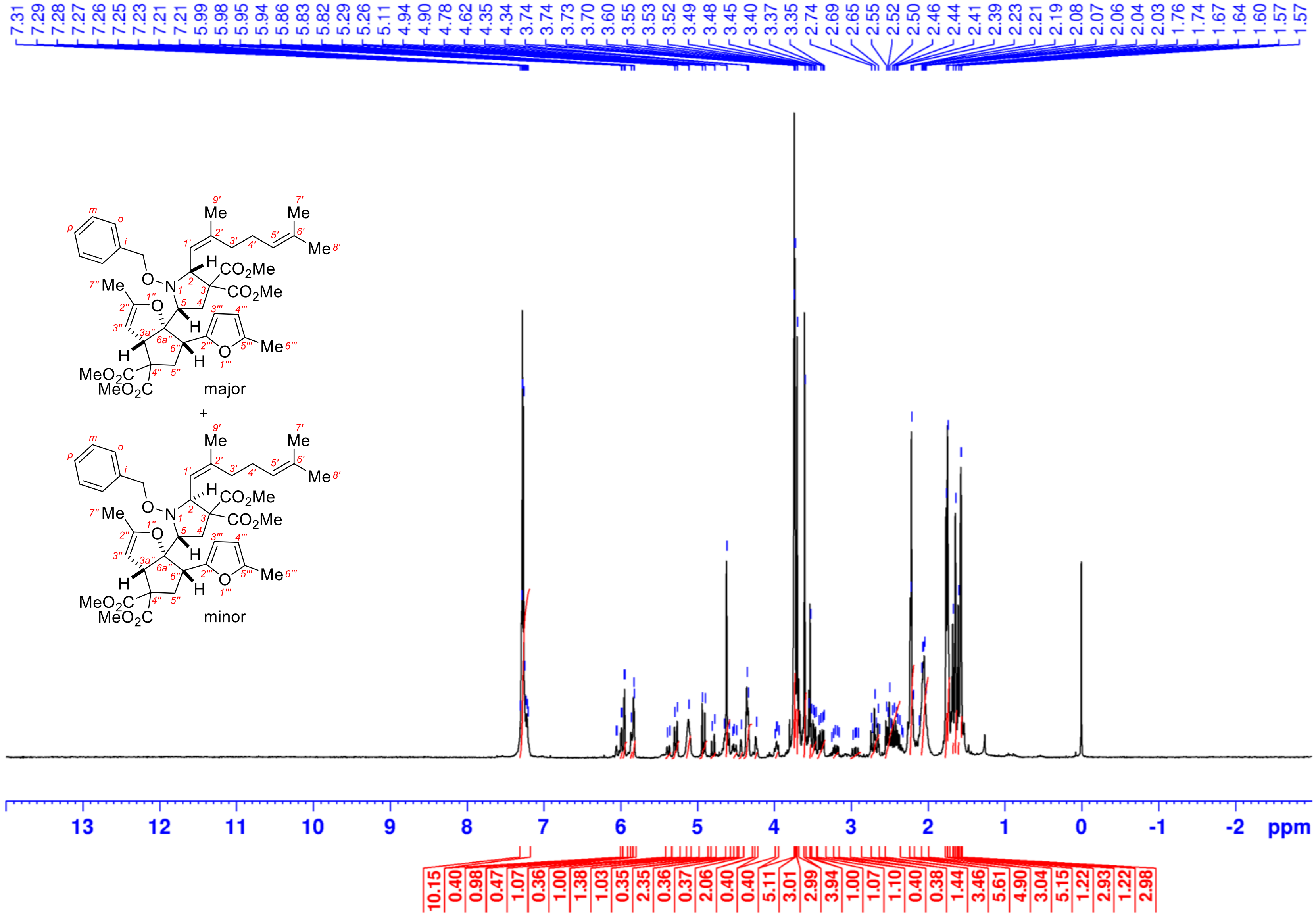




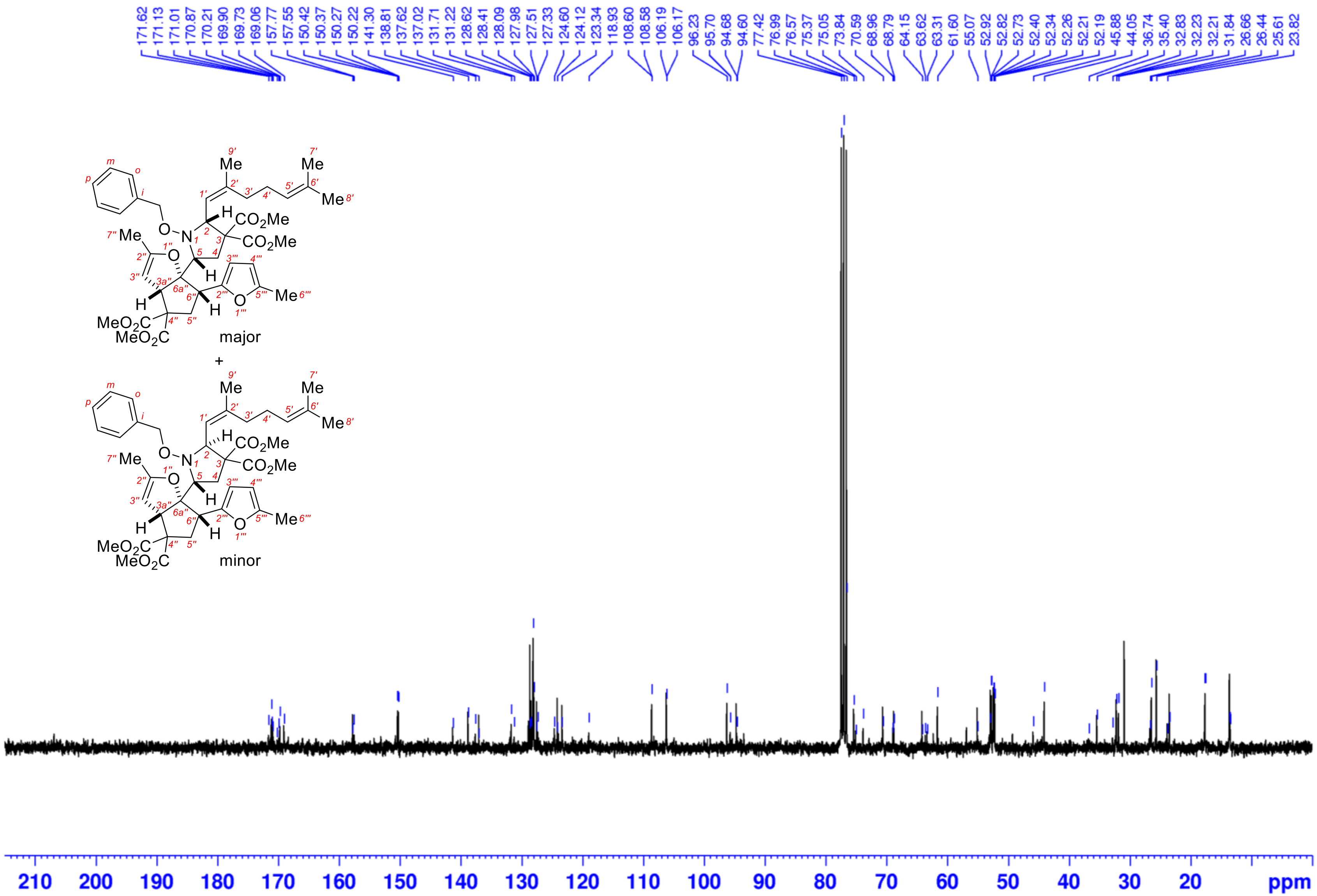
$^1H,^{13}C$-edited-HSQC NMR spectrum of (2*RS*,5*SR*)-**11** ($^1H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

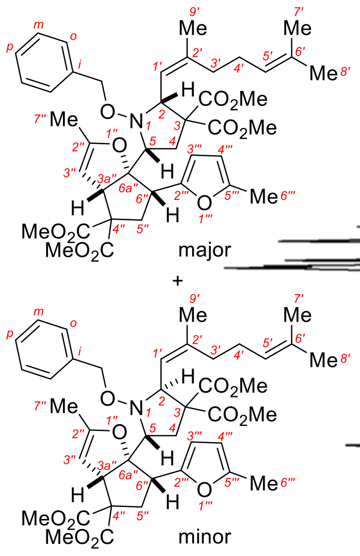
$^{1}H,^{13}C$-HMBC NMR spectrum of (2*RS*,5*SR*)-**11** ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)

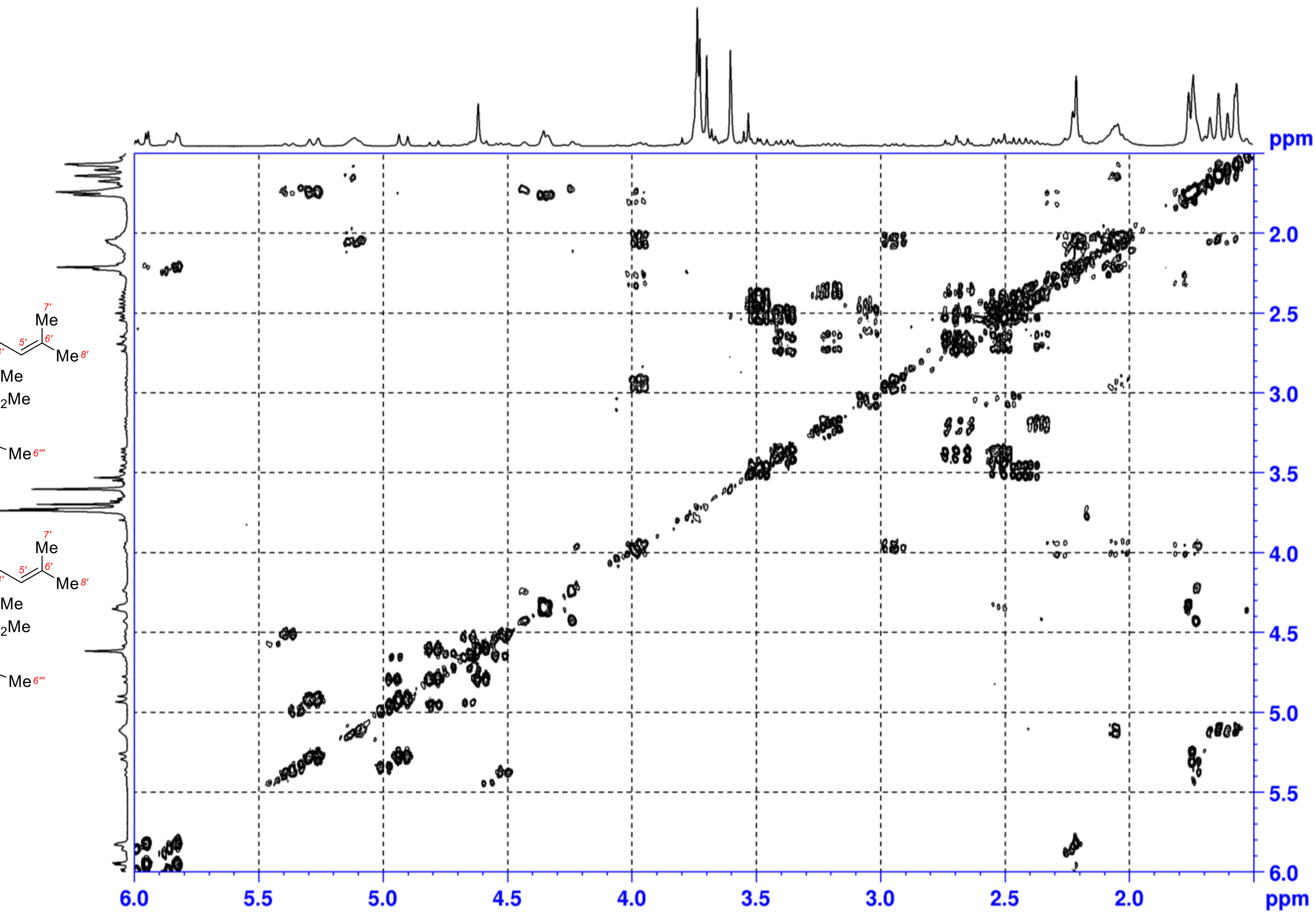


$^{1}$H NMR spectrum of **11**, (2*RS*,5*RS*)/(2*RS*,5*SR*) 2.8:1 (300.1 MHz, $CDCl_3$)

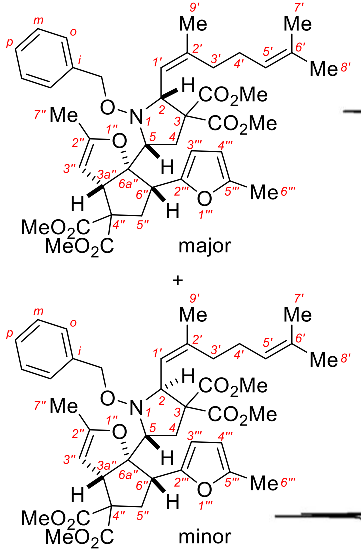


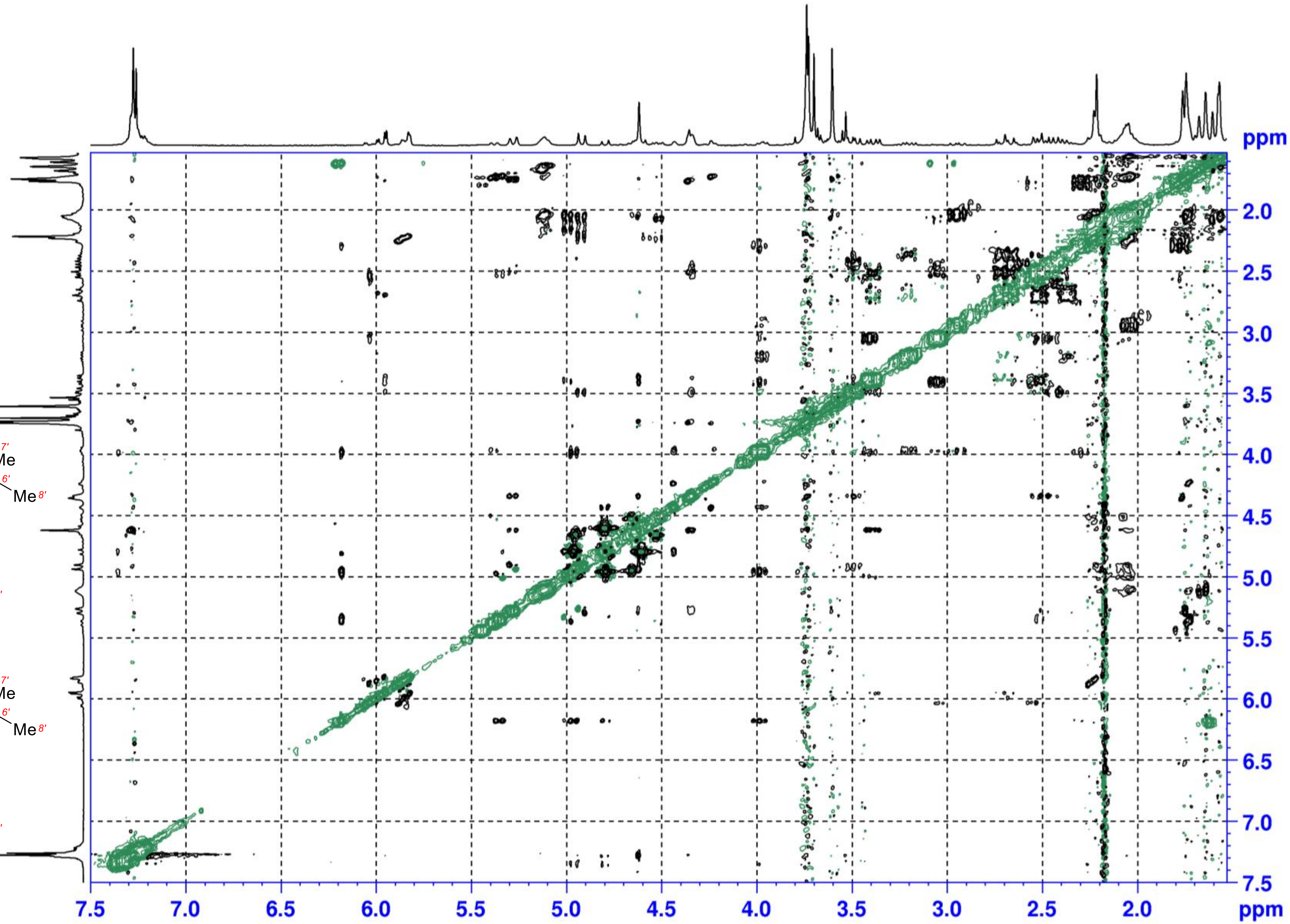

$^{13}$C NMR spectrum of **11**, (2*RS*,5*RS*)/(2*RS*,5*SR*) 2.8:1 (75.5 MHz, $CDCl_3$)



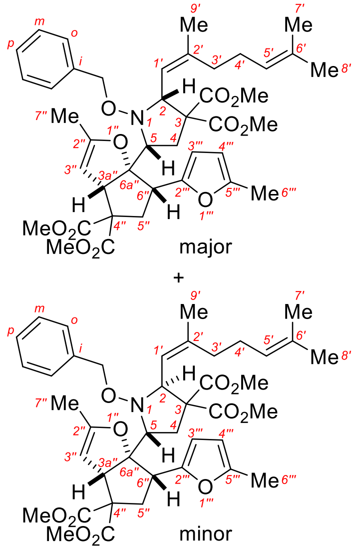



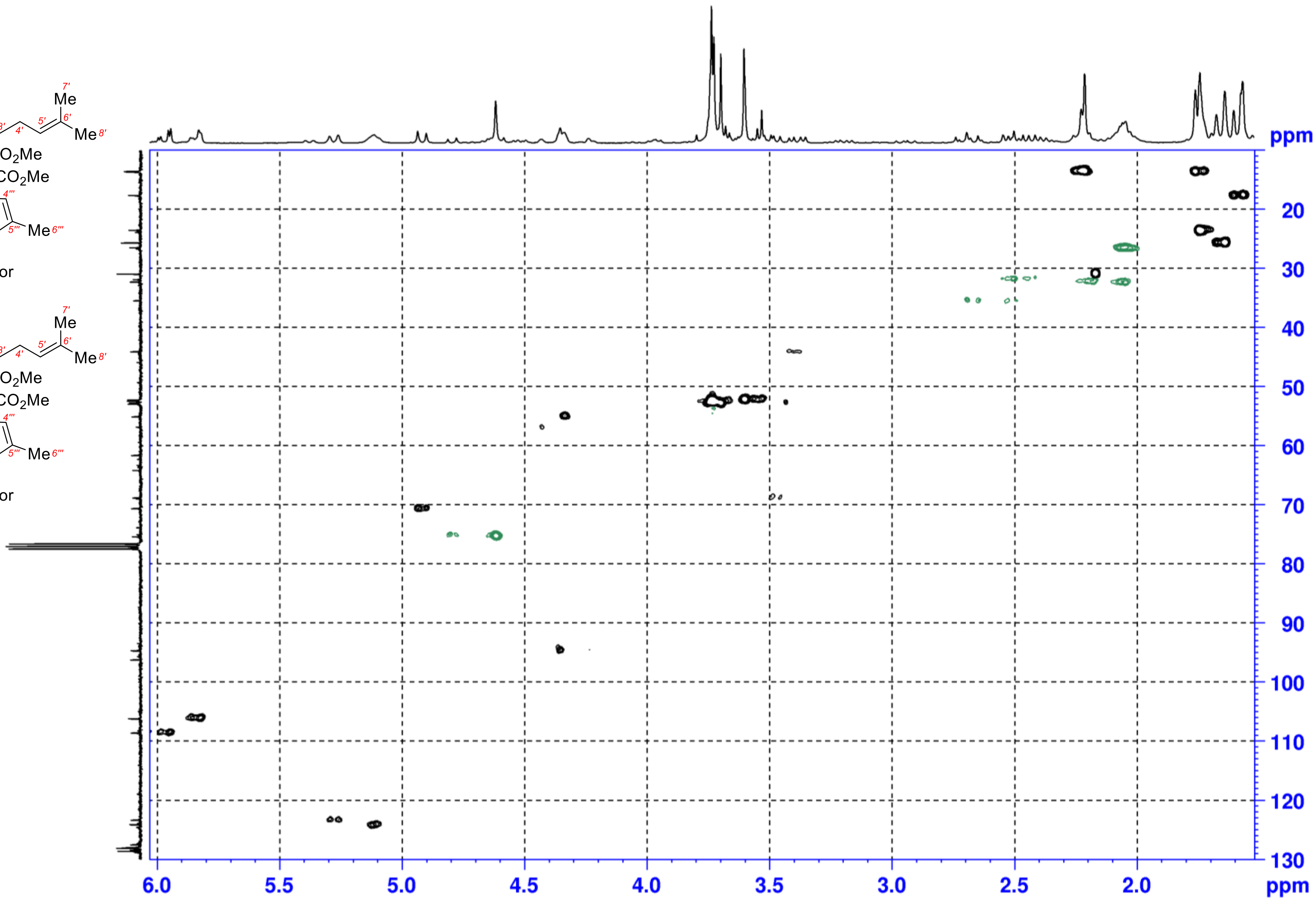

[1]H,[1]H-COSY NMR spectrum of **11**, (2*RS*,5*RS*)/(2*RS*,5*SR*) 2.8:1 (300.1 MHz, $CDCl_3$)



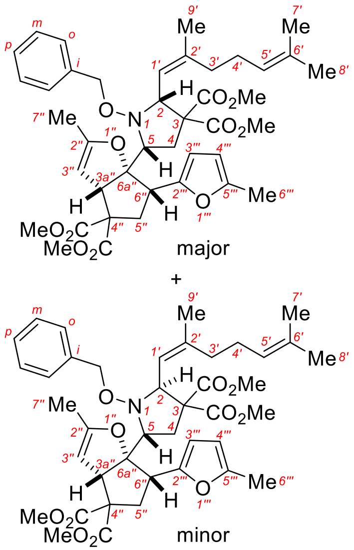



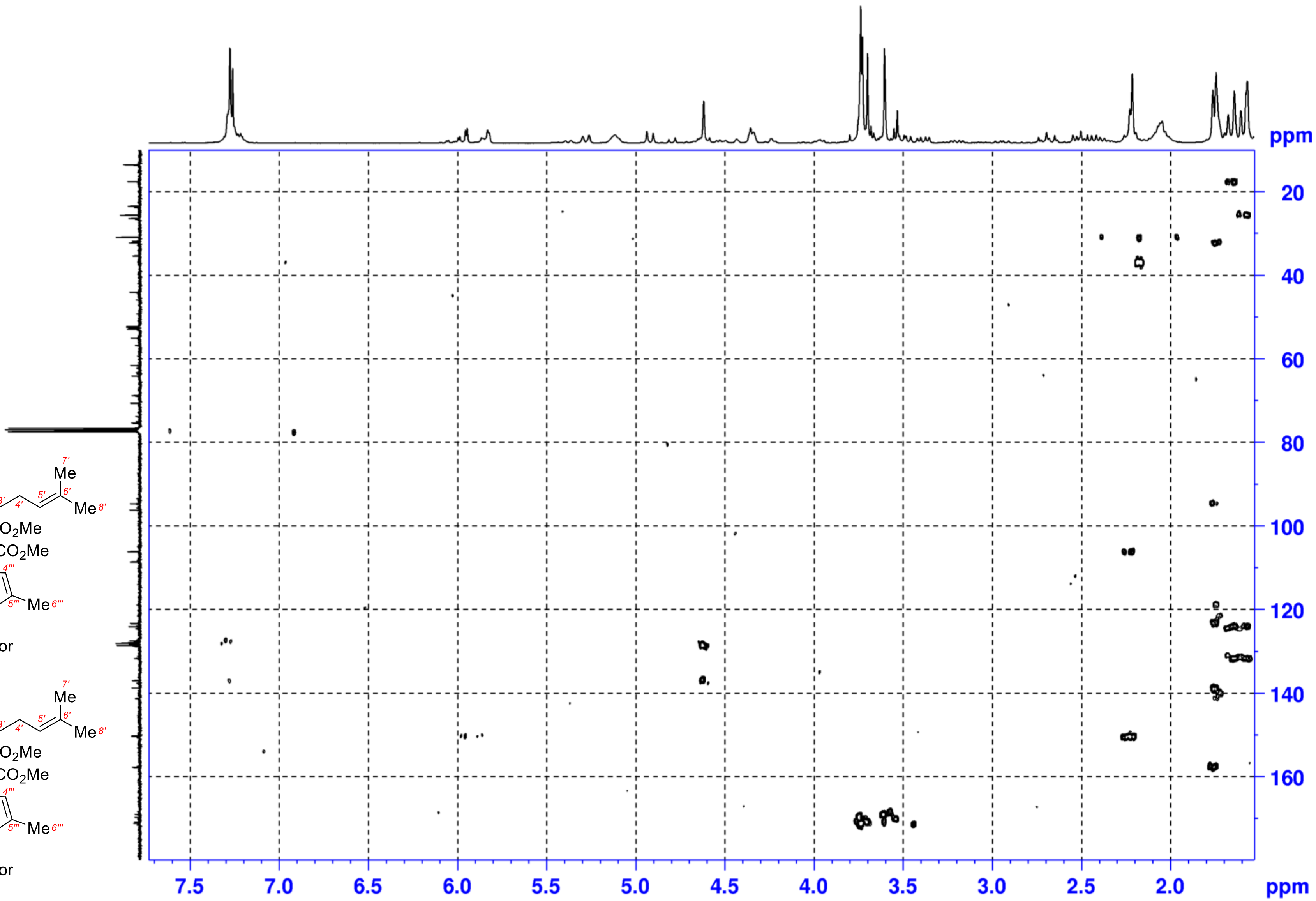

[1]H,[1]H-NOESY NMR spectrum of **11**, (2*RS*,5*RS*)/(2*RS*,5*SR*) 2.8:1 (300.1 MHz, $CDCl_3$)



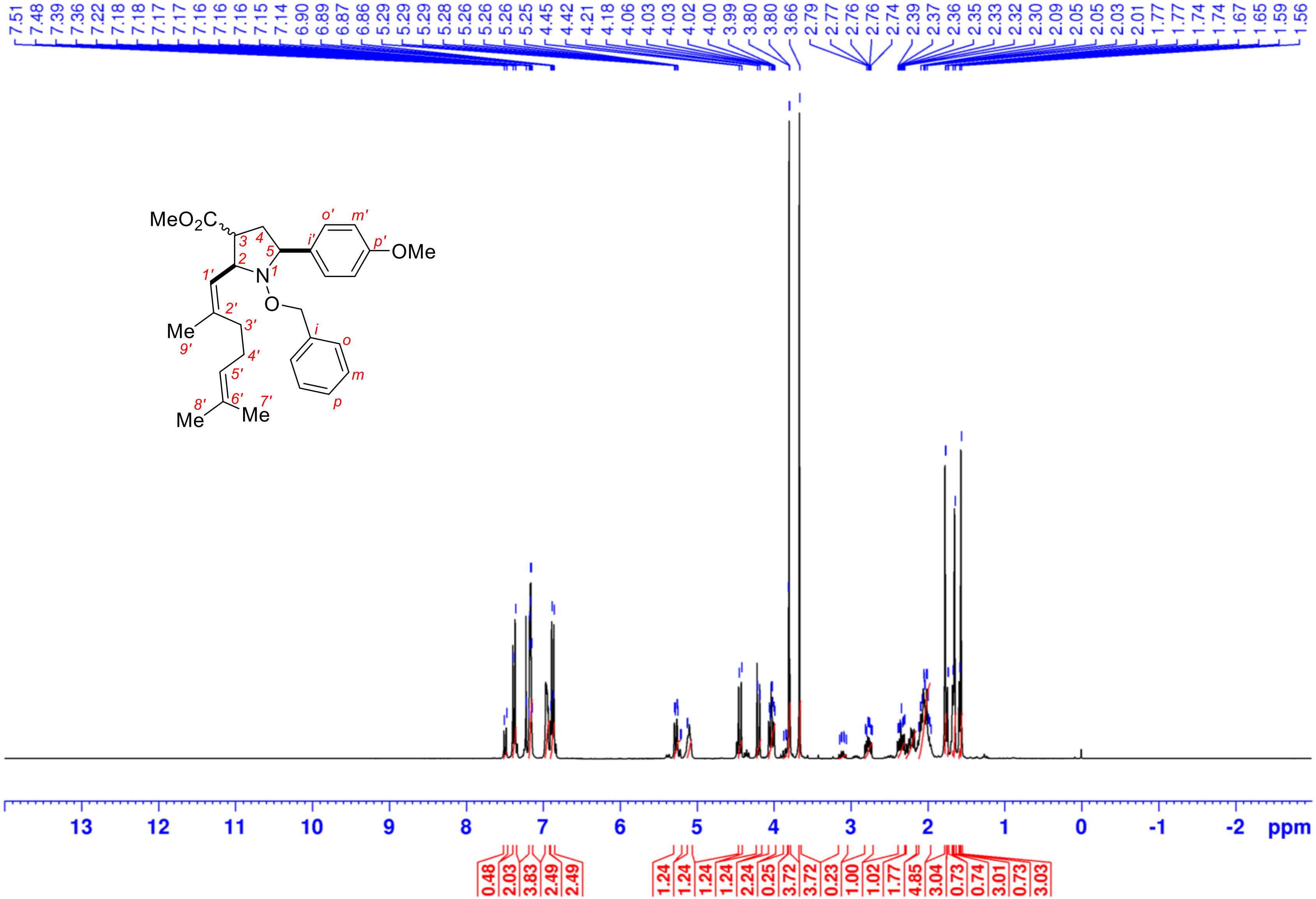



[1]H,[13]C-edited-HSQC NMR spectrum of **11**, (2*RS*,5*RS*)/(2*RS*,5*SR*) 2.8:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

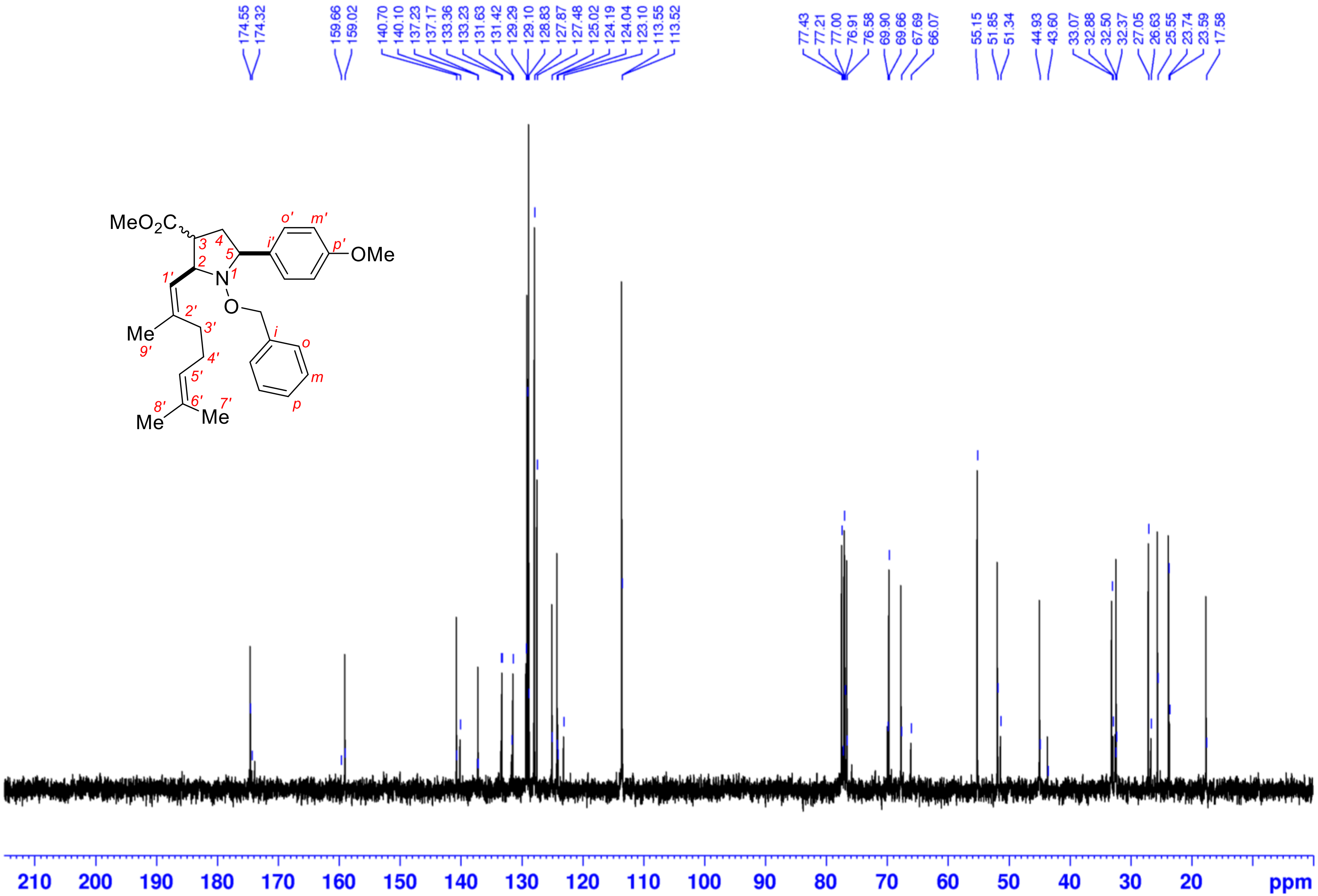


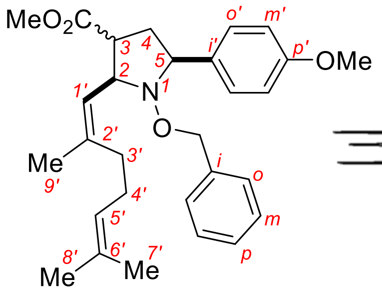

[1]H,[13]C-HMBC NMR spectrum of **11**, (2*RS*,5*RS*)/(2*RS*,5*SR*) 2.8:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)

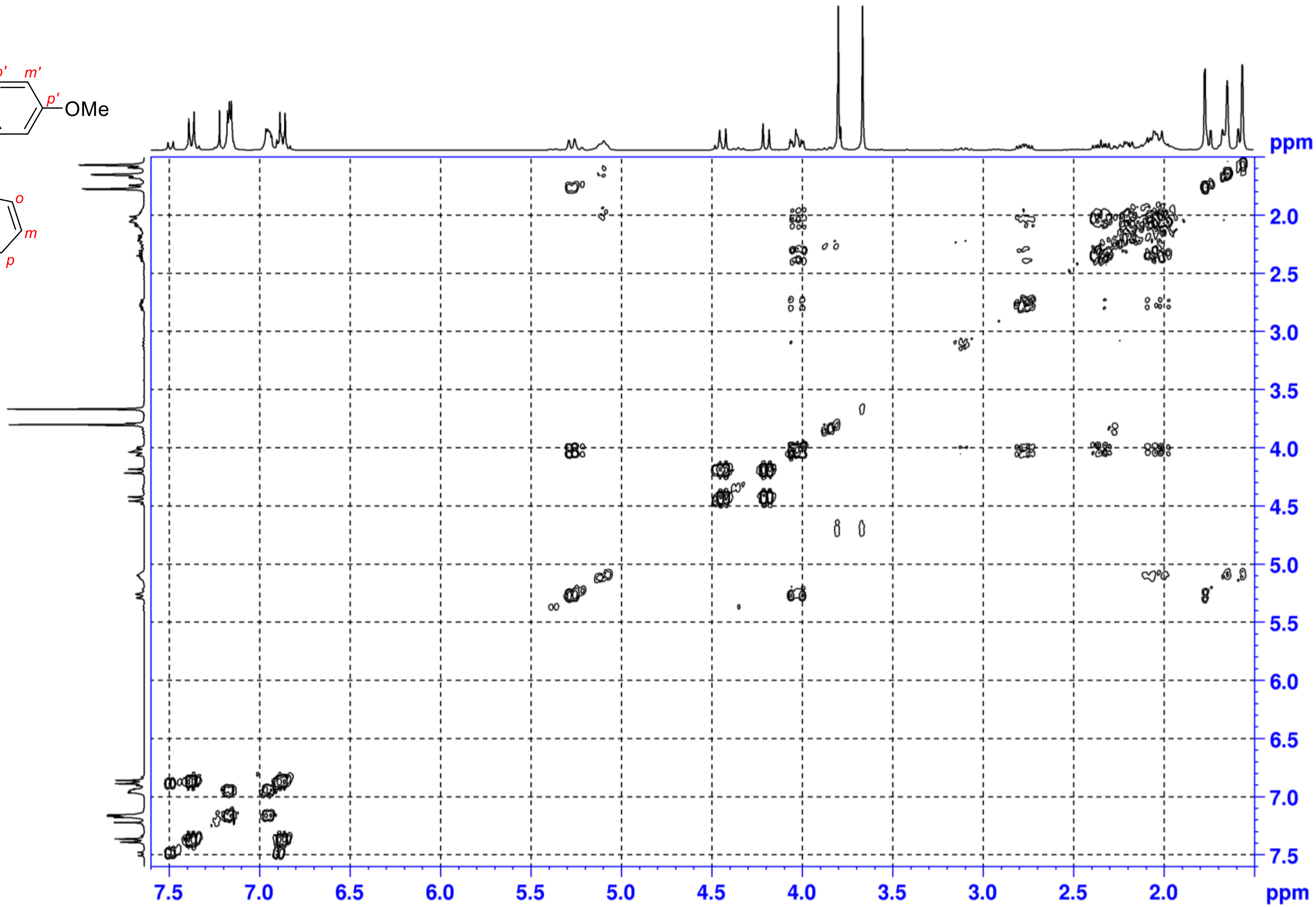


[1]H NMR spectrum of **12**, *trans,trans*/*cis,cis* 4.3:1 (300.1 MHz, $CDCl_3$)

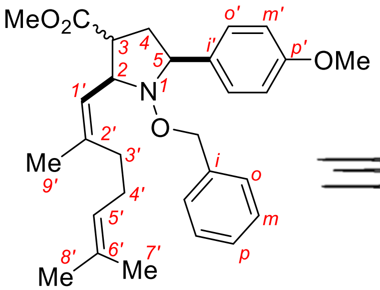


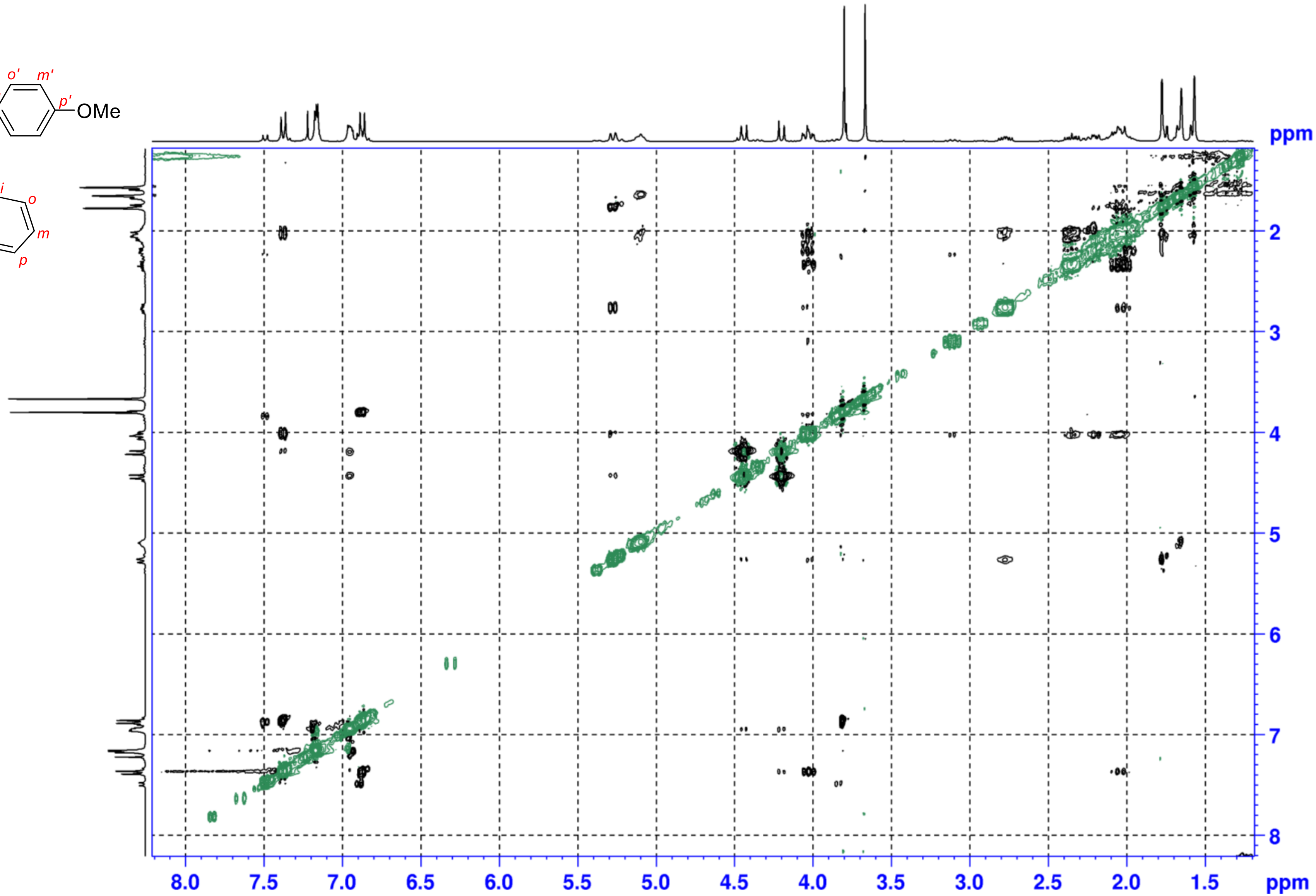

$^{13}C$ NMR spectrum of **12**, *trans,trans*/*cis,cis* 4.3:1 (75.5 MHz, $CDCl_3$)



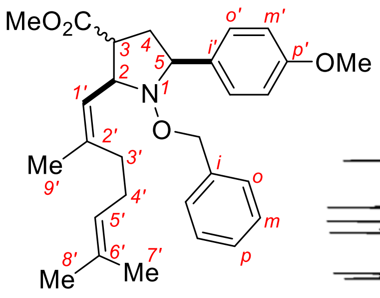



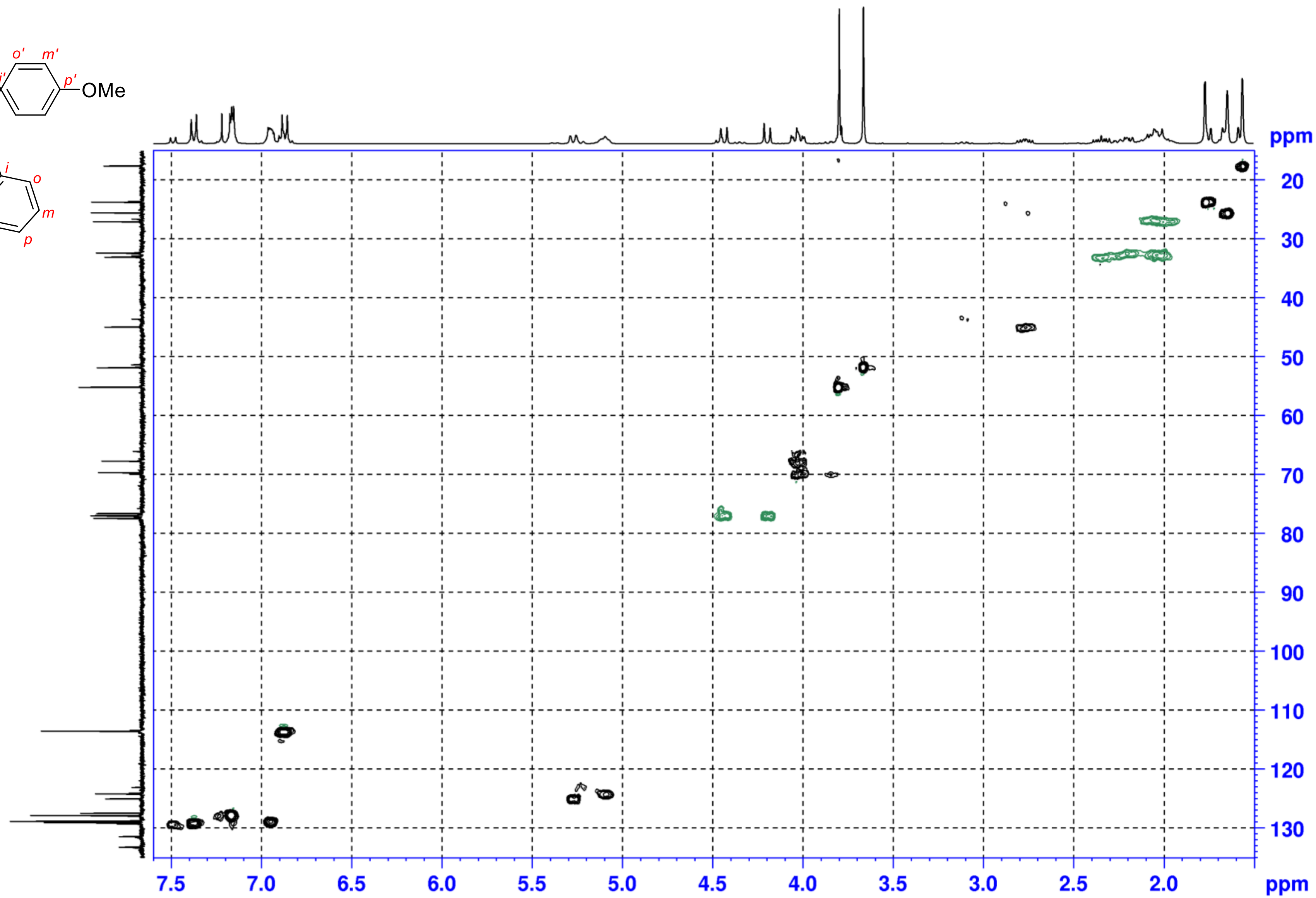

$^{1}H,^{1}H$-COSY NMR spectrum of **12**, *trans,trans*/*cis,cis* 4.3:1 (300.1 MHz, $CDCl_3$)



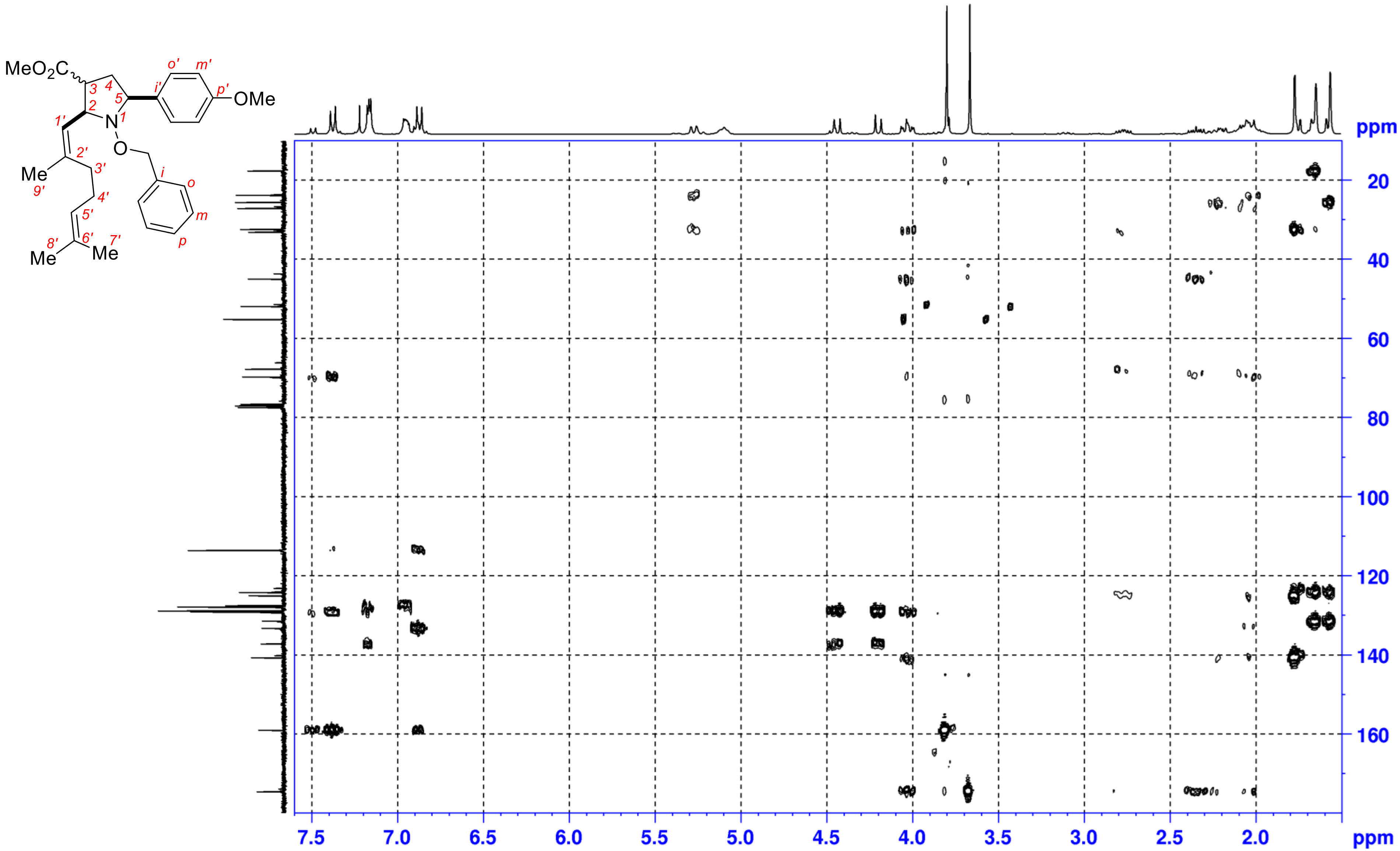




$^1$H,$^1$H-NOESY NMR spectrum of **12**, *trans,trans*/*cis,cis* 4.3:1 (300.1 MHz, $CDCl_3$)

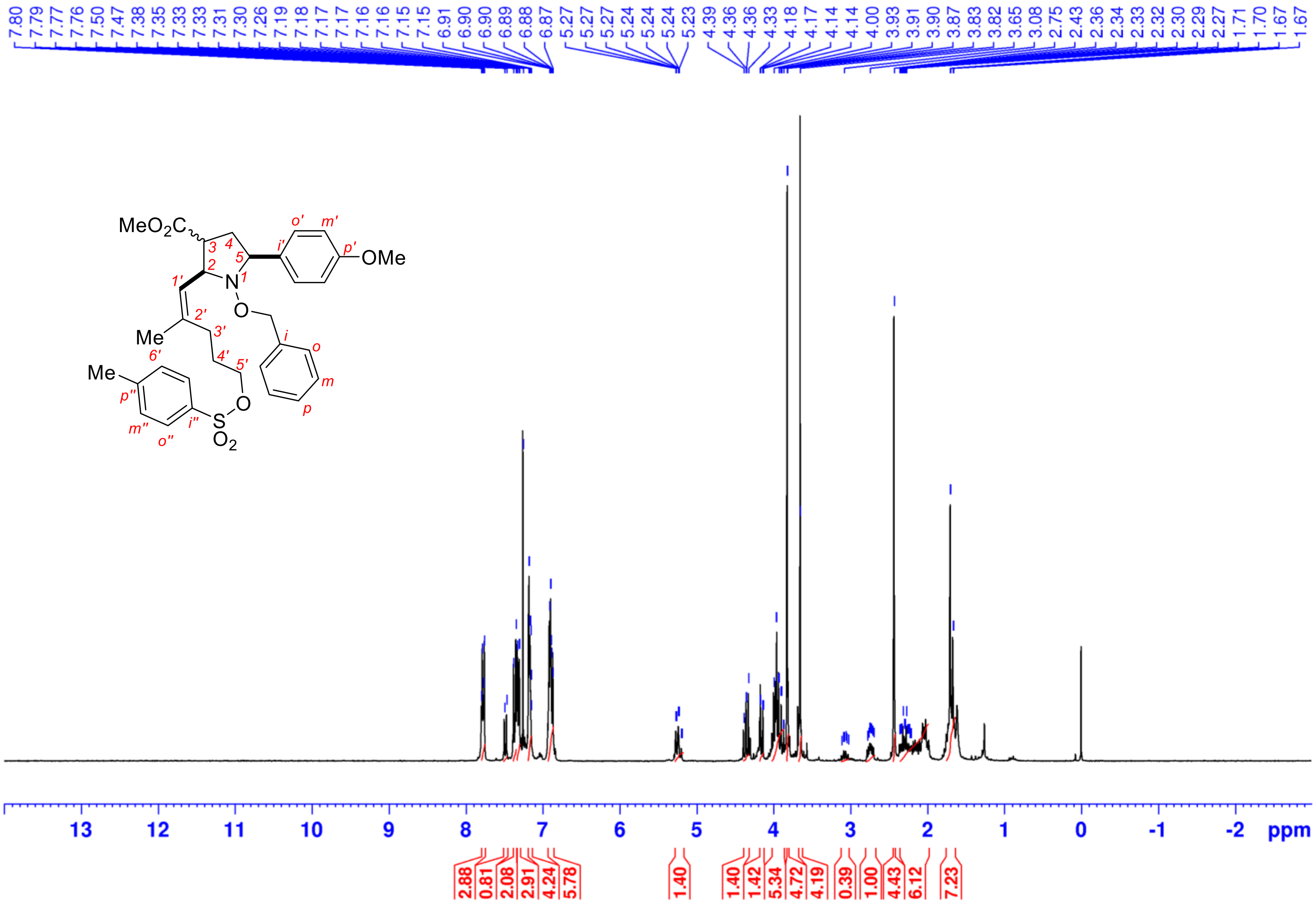


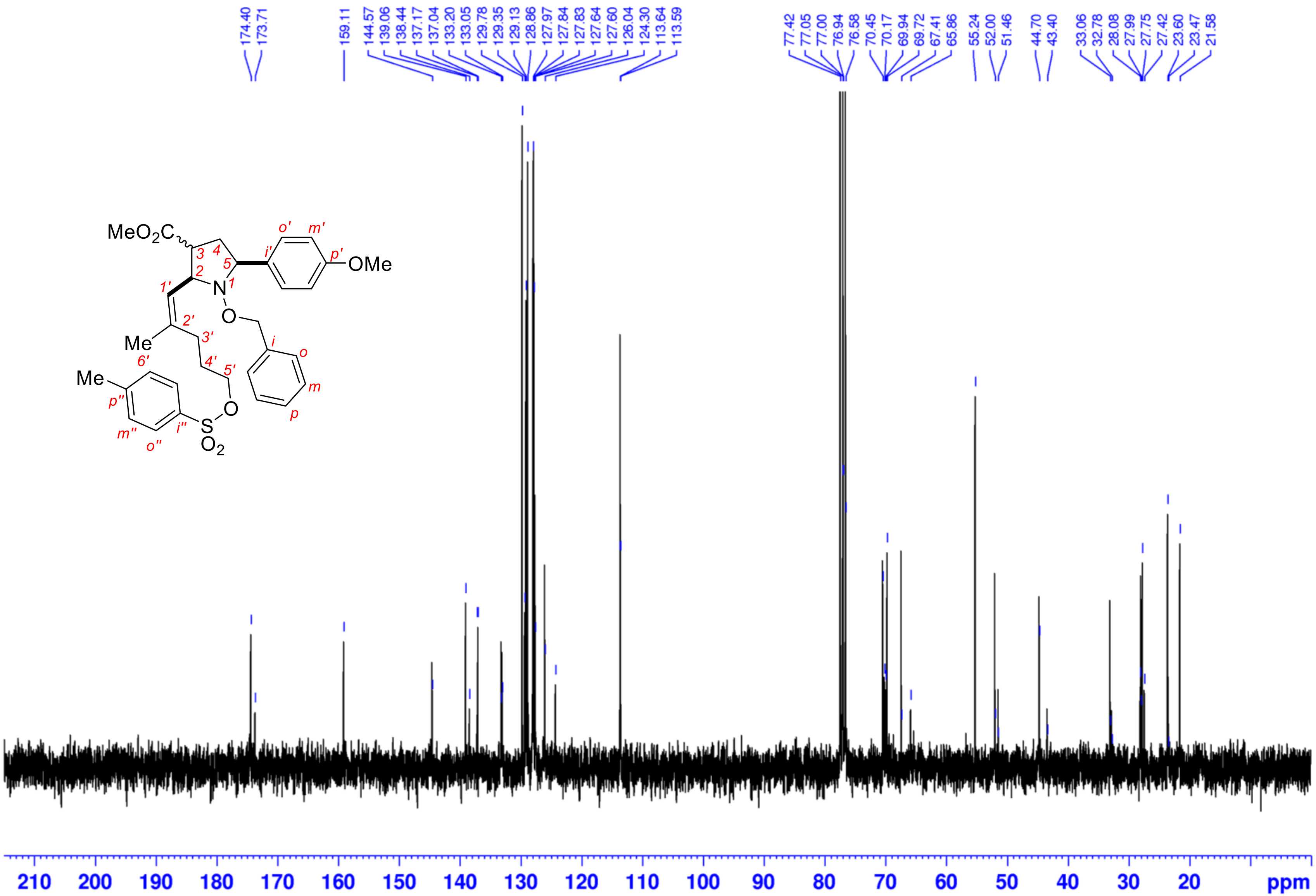

$^{1}H,^{13}C$-edited-HSQC NMR spectrum of **12**, *trans,trans*/*cis,cis* 4.3:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)



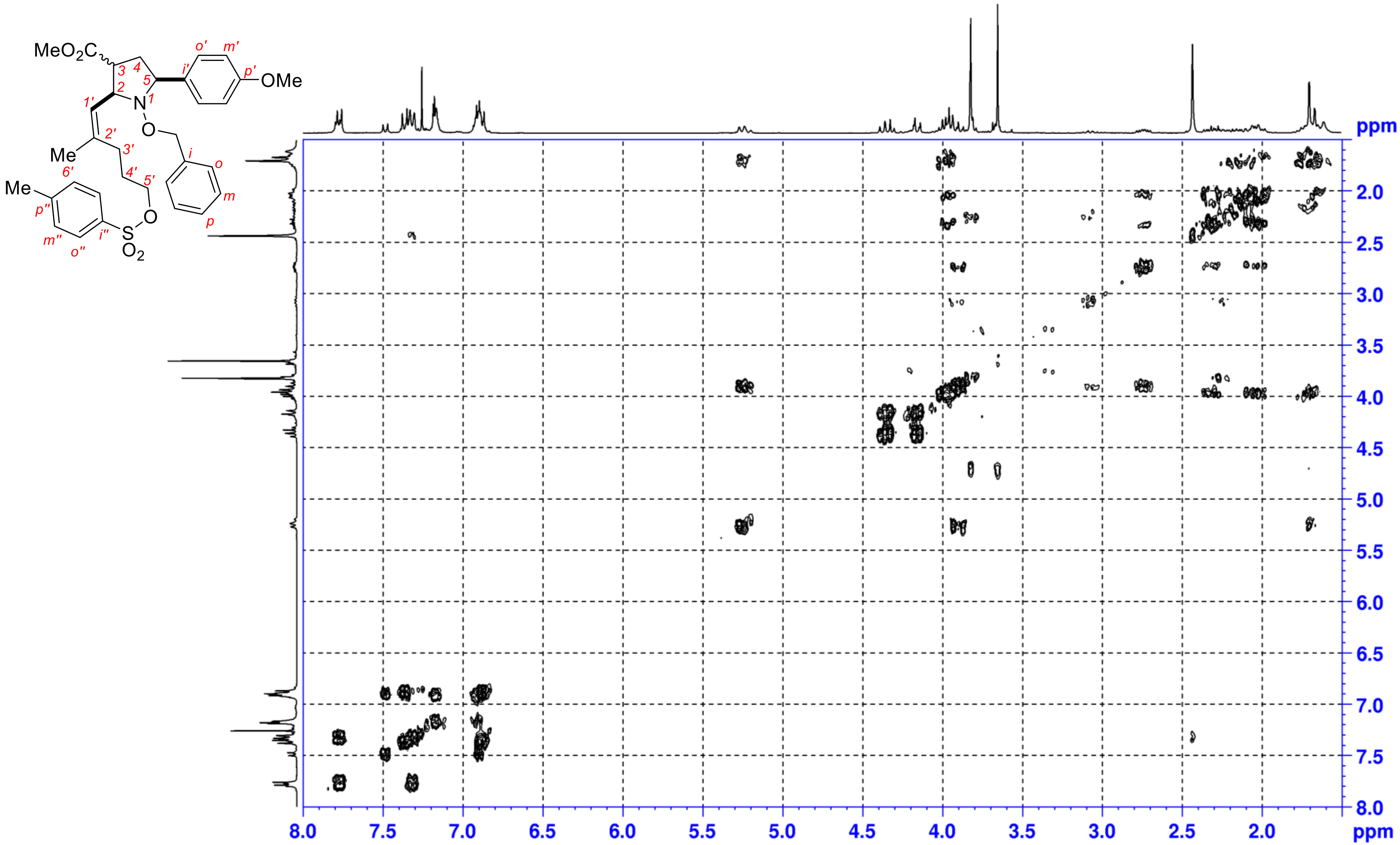

$^{1}H,^{13}C$-HMBC NMR spectrum of **12**, *trans,trans*/*cis,cis* 4.3:1 ($^{1}H$: 300.1 MHz; $^{13}C$: 75.5 MHz; $CDCl_3$)



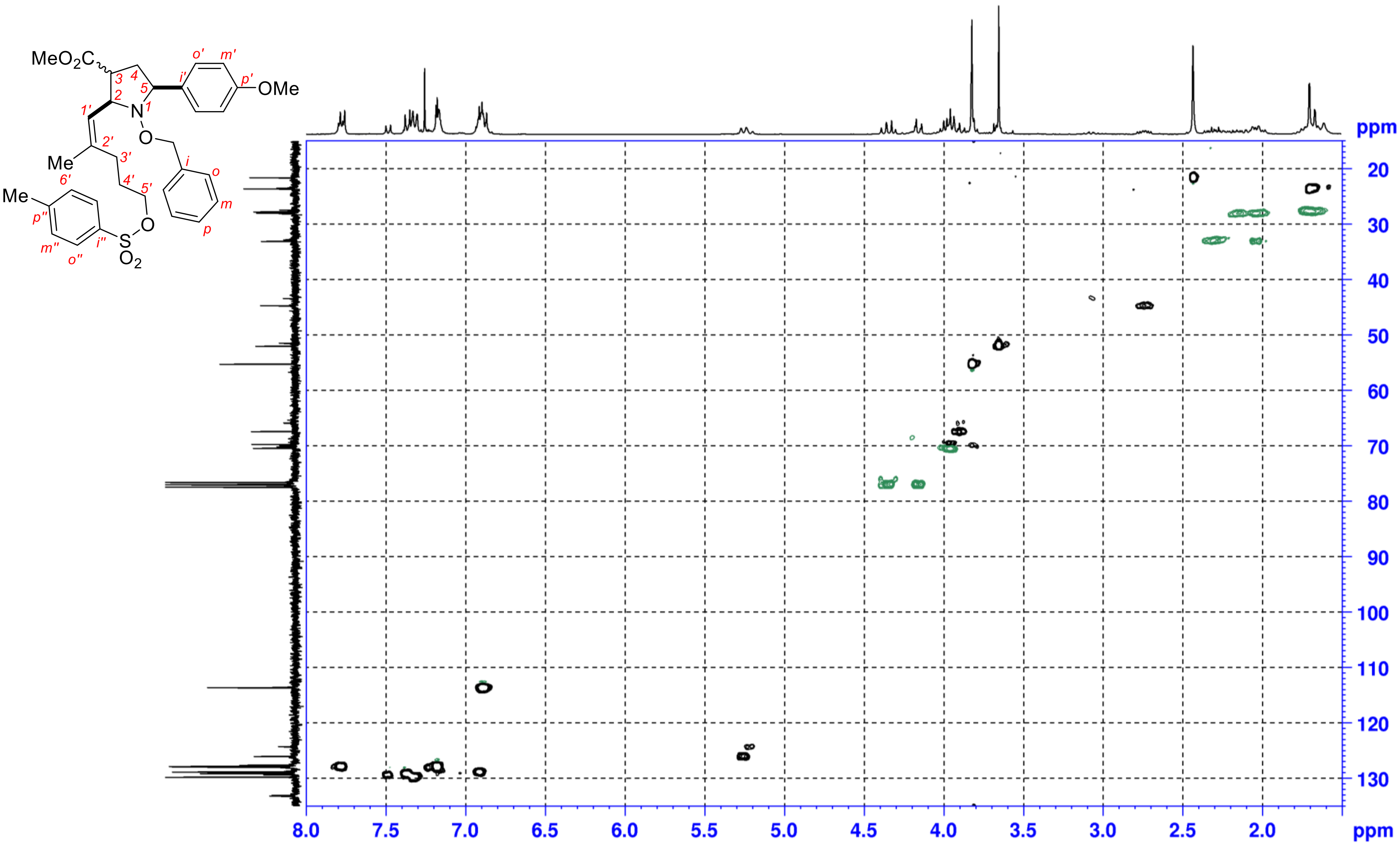

[1]H NMR spectrum of **13**, dr 2.6:1 (300.1 MHz, $CDCl_3$)



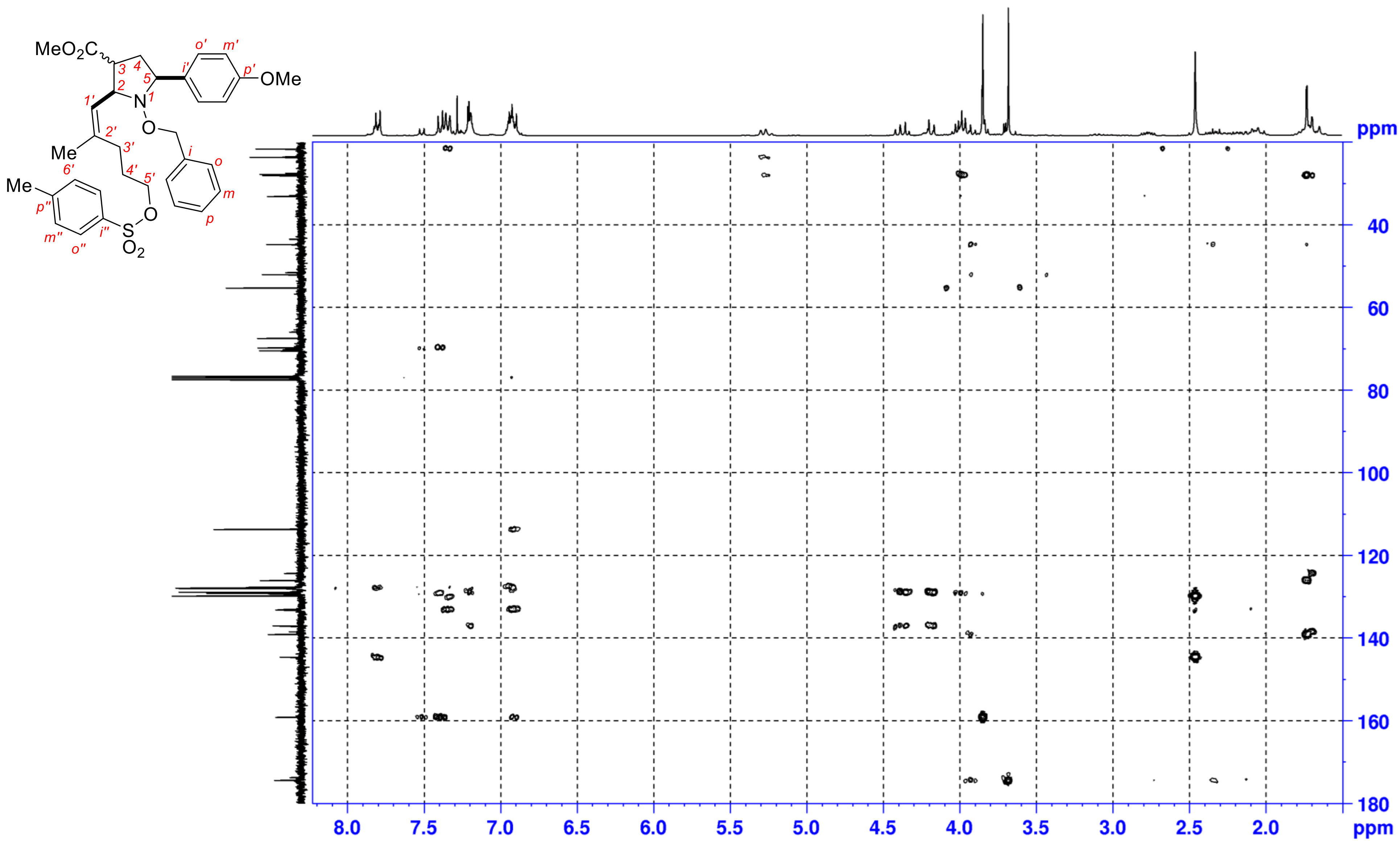

$^{13}$C NMR spectrum of **13**, dr 2.6:1 (75.5 MHz, $CDCl_3$)



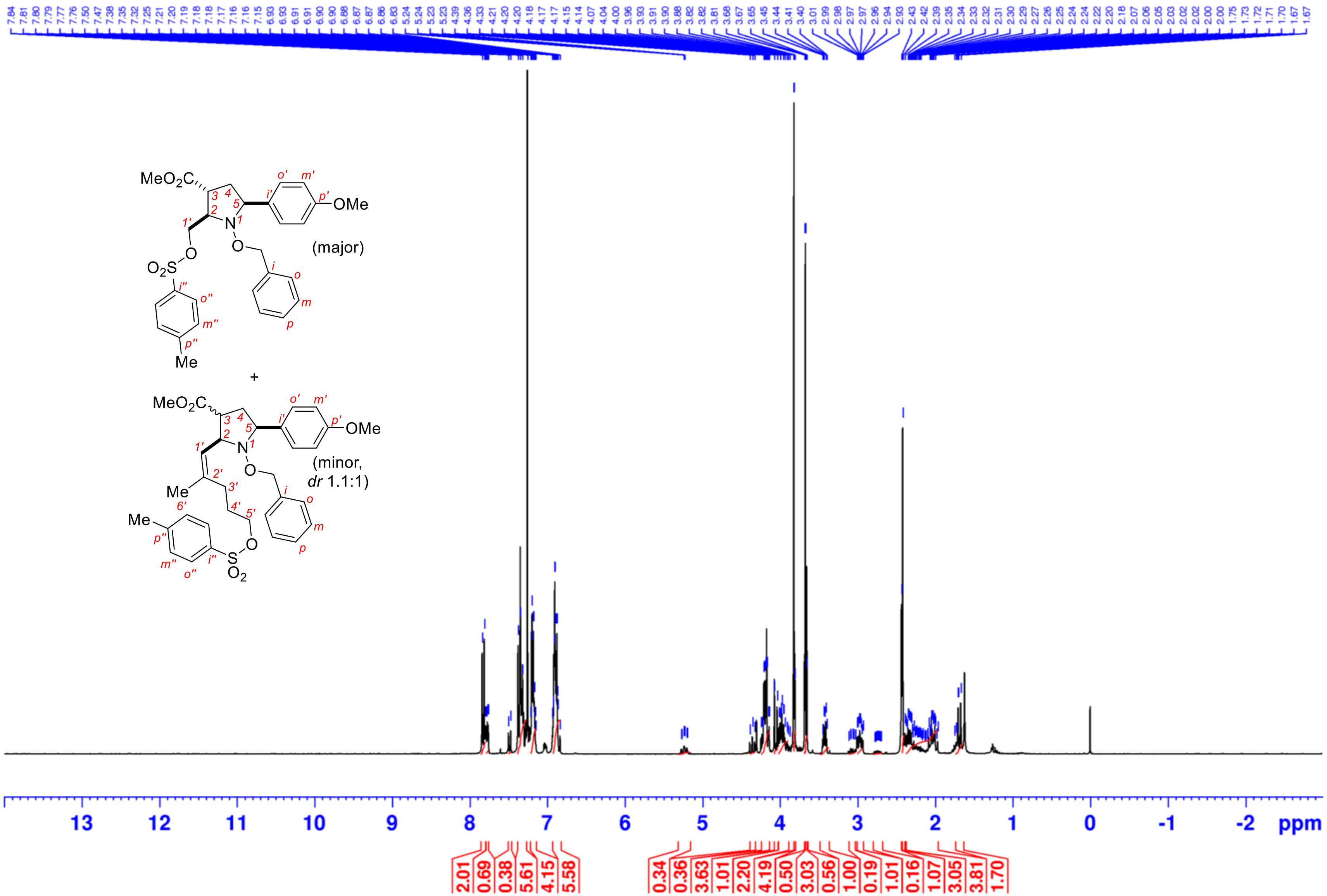

$^{1}$H,$^{1}$H-COSY NMR spectrum of **13**, dr 2.6:1 (300.1 MHz, $CDCl_3$)



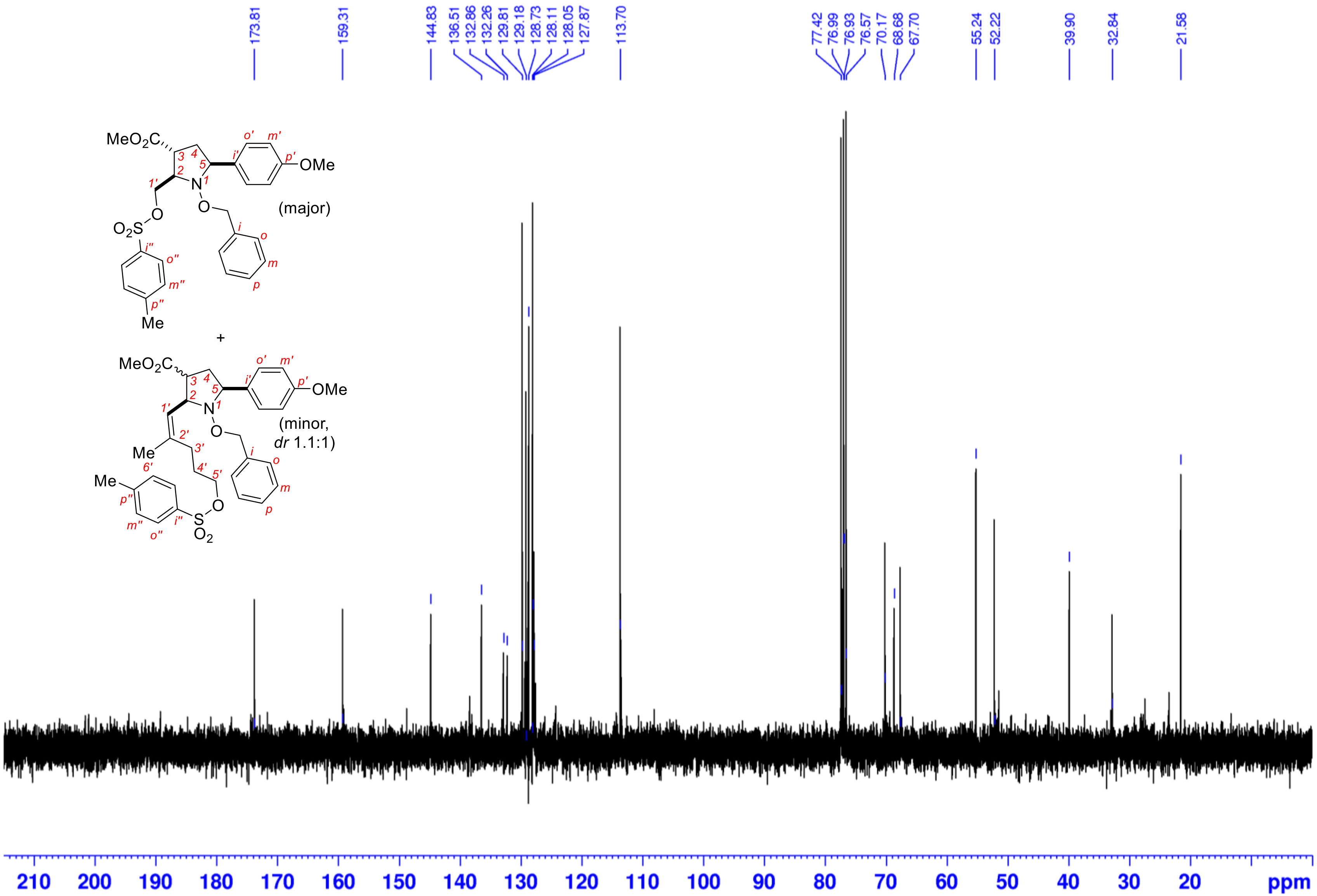

[1]H,[13]C-edited-HSQC NMR spectrum of **13**, dr 2.6:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)



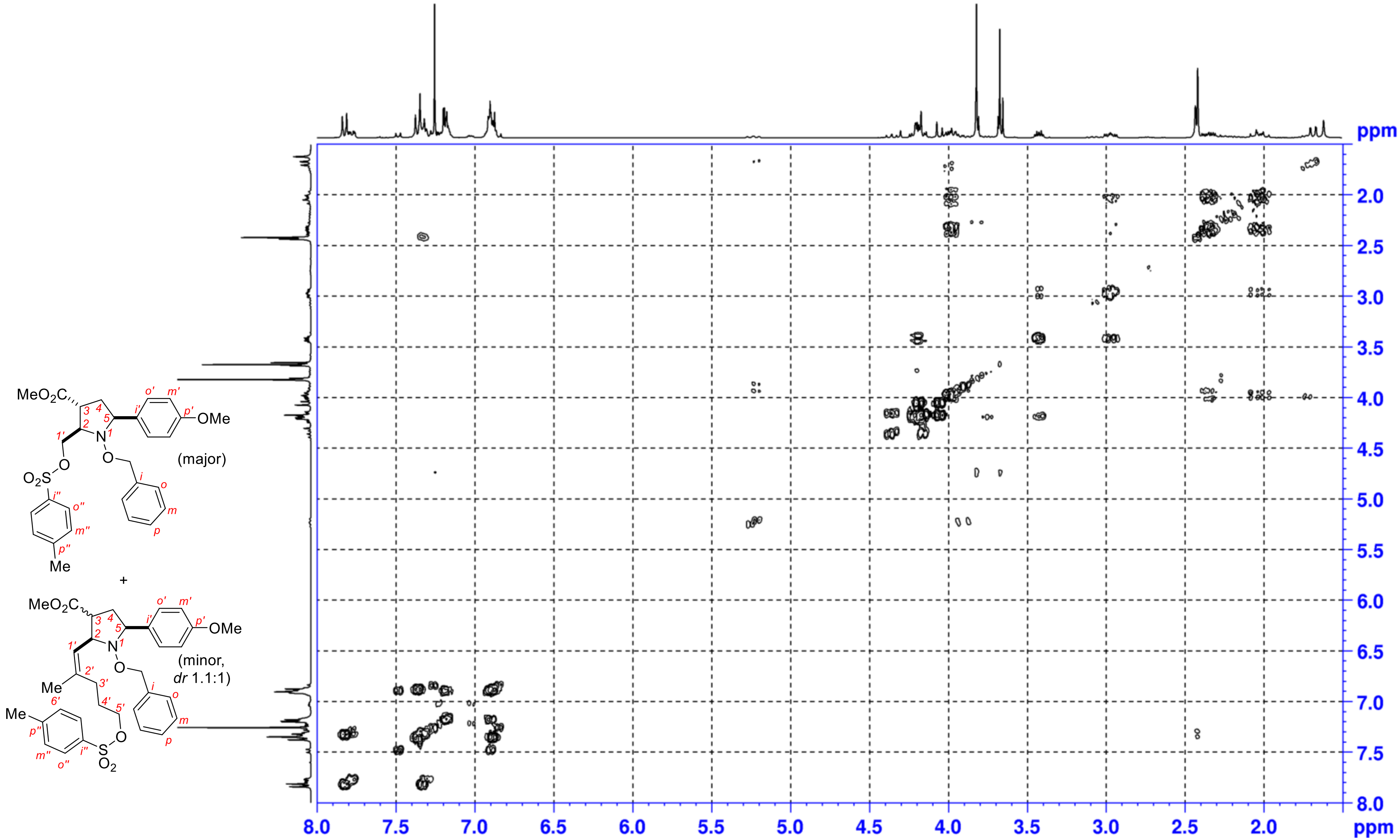

[1]H,[13]C-HMBC NMR spectrum of **13**, dr 2.6:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)



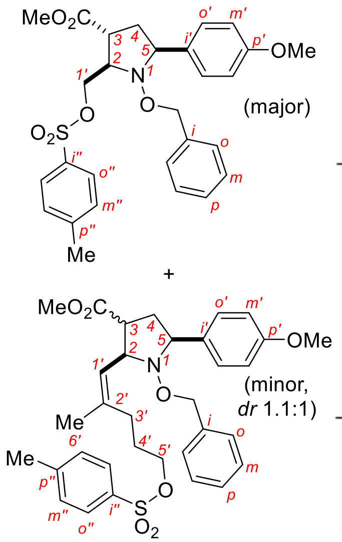
$^{1}H$ NMR spectrum of **14**/**13**, 3:1 (300.1 MHz, $CDCl_3$)

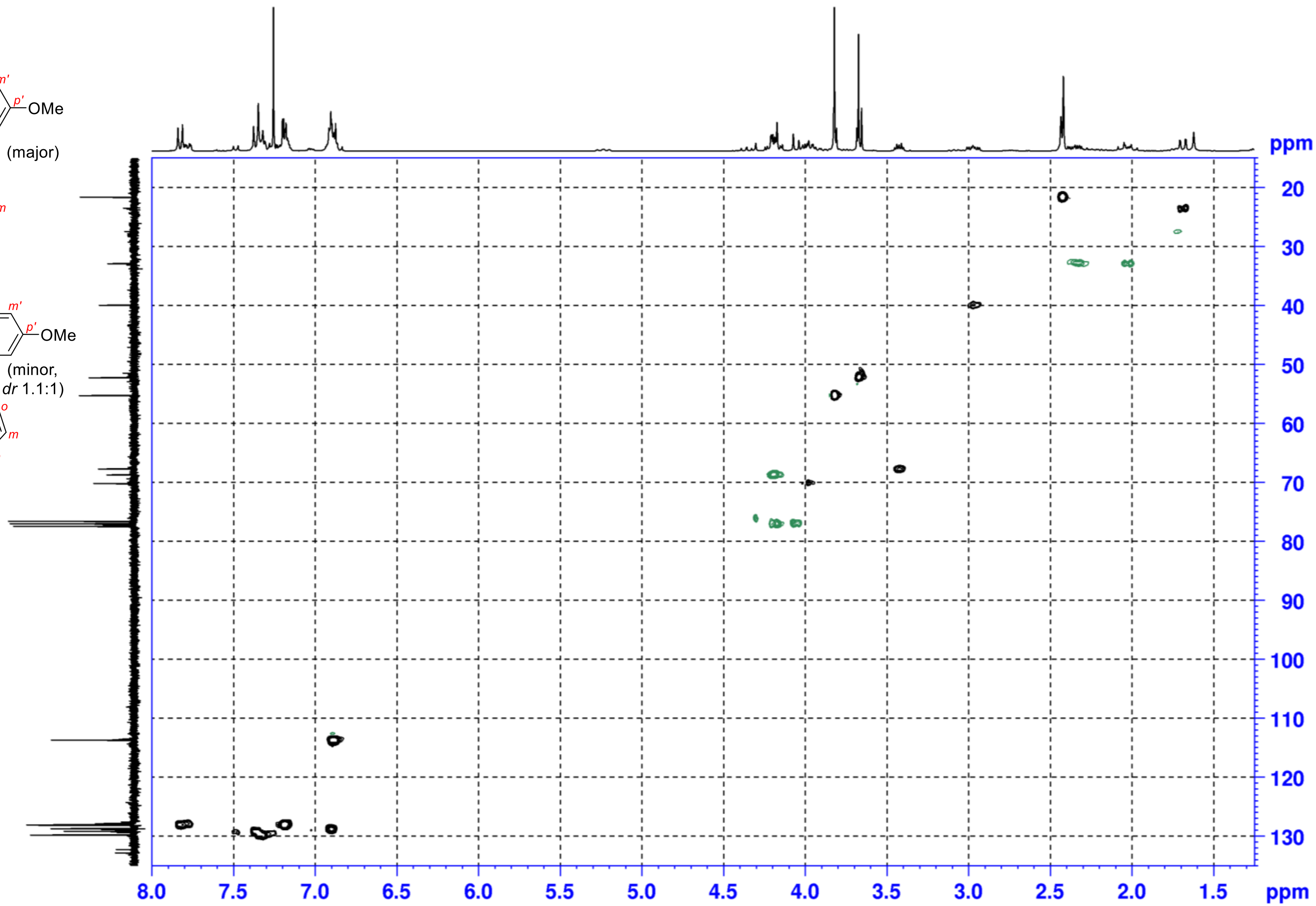



$^{13}$C NMR spectrum of **14**/**13**, 3:1 (75.5 MHz, $CDCl_3$)

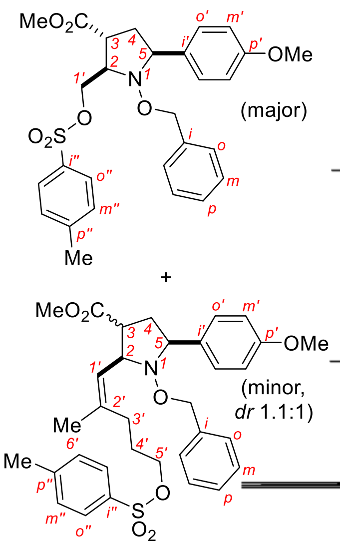


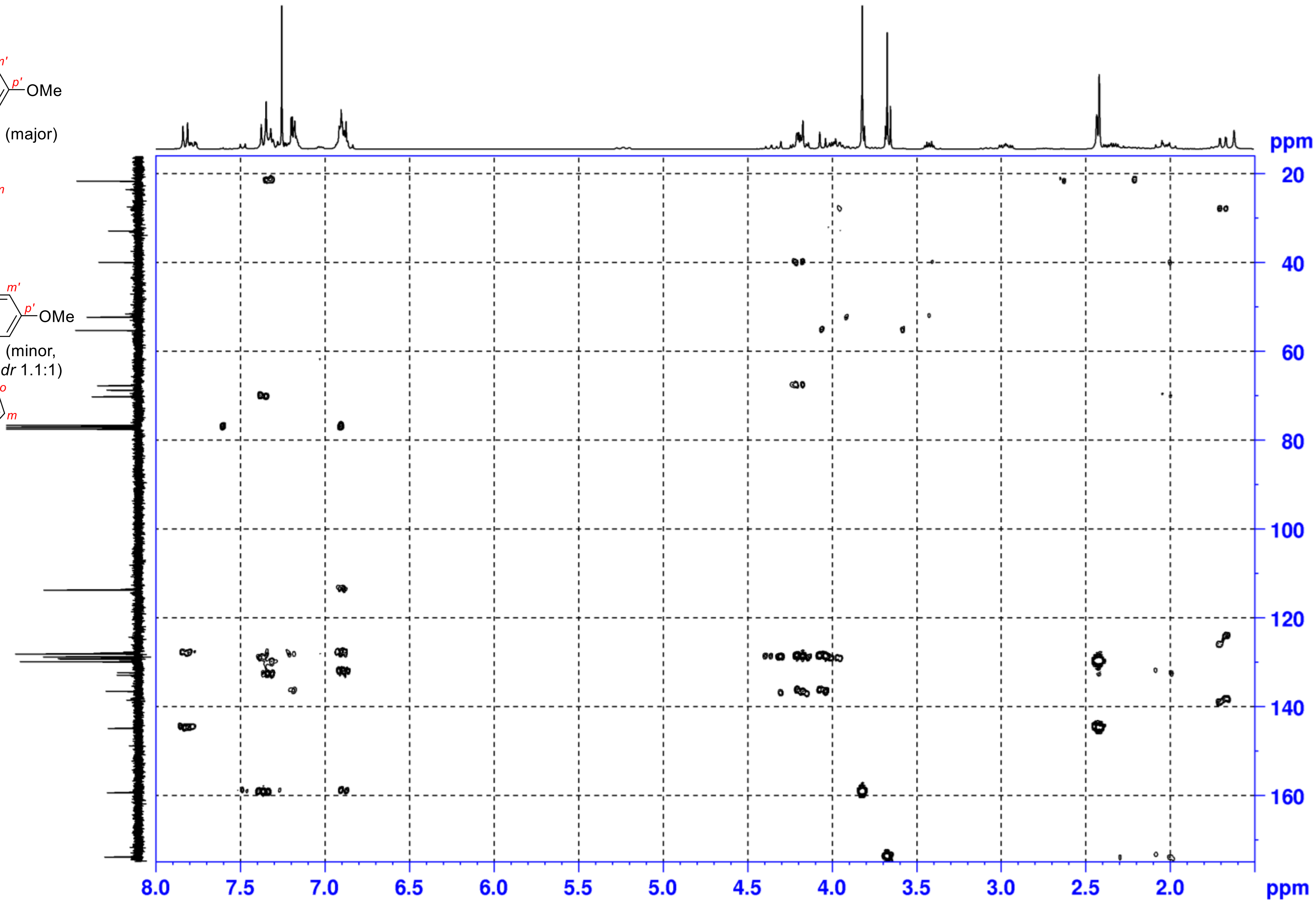

$^{1}H,^{1}H$-COSY NMR spectrum of **14**/**13**, 3:1 (300.1 MHz, $CDCl_3$)



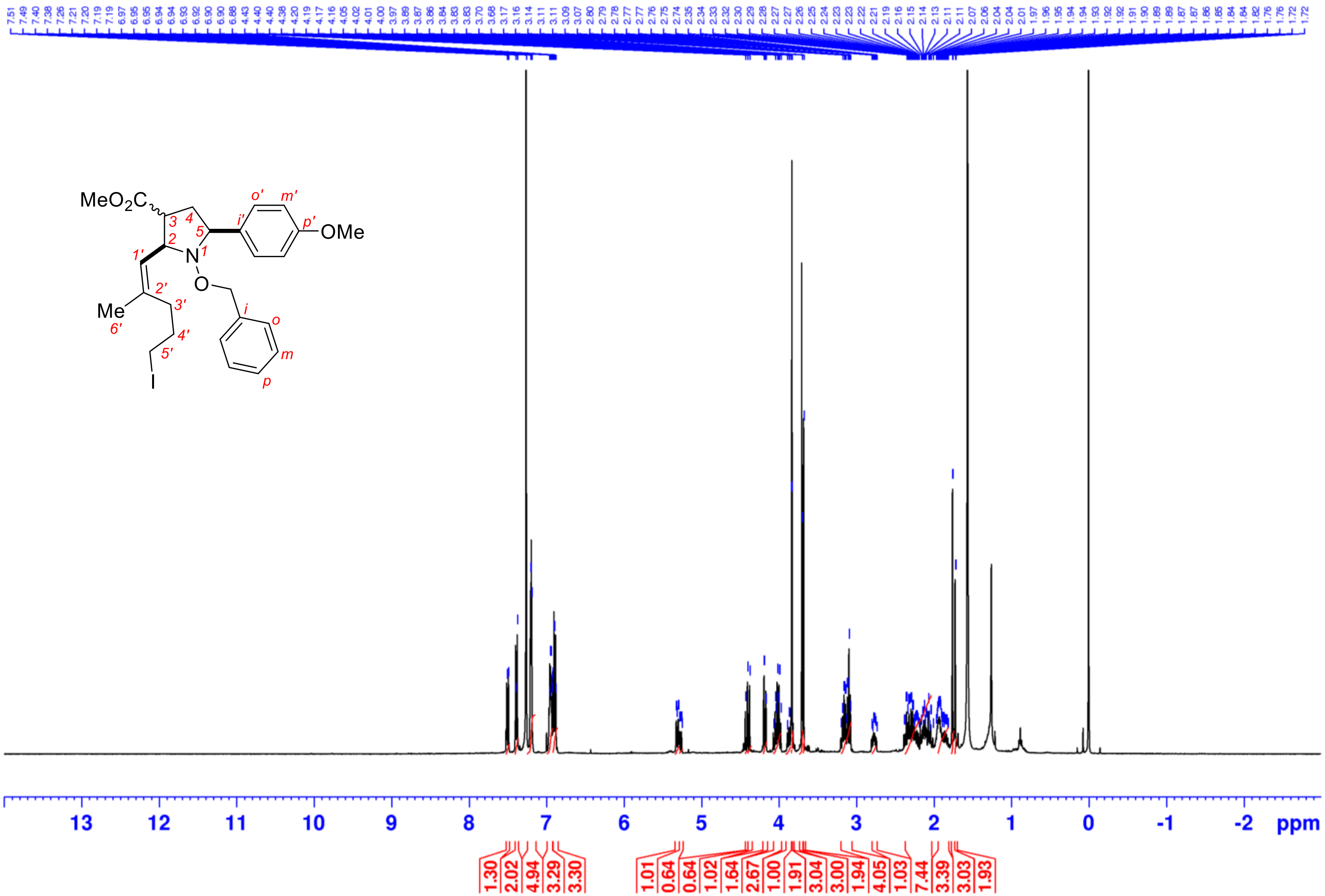




$^{1}$H,$^{13}$C-edited-HSQC NMR spectrum of **14**/**13**, 3:1 ($^{1}$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)

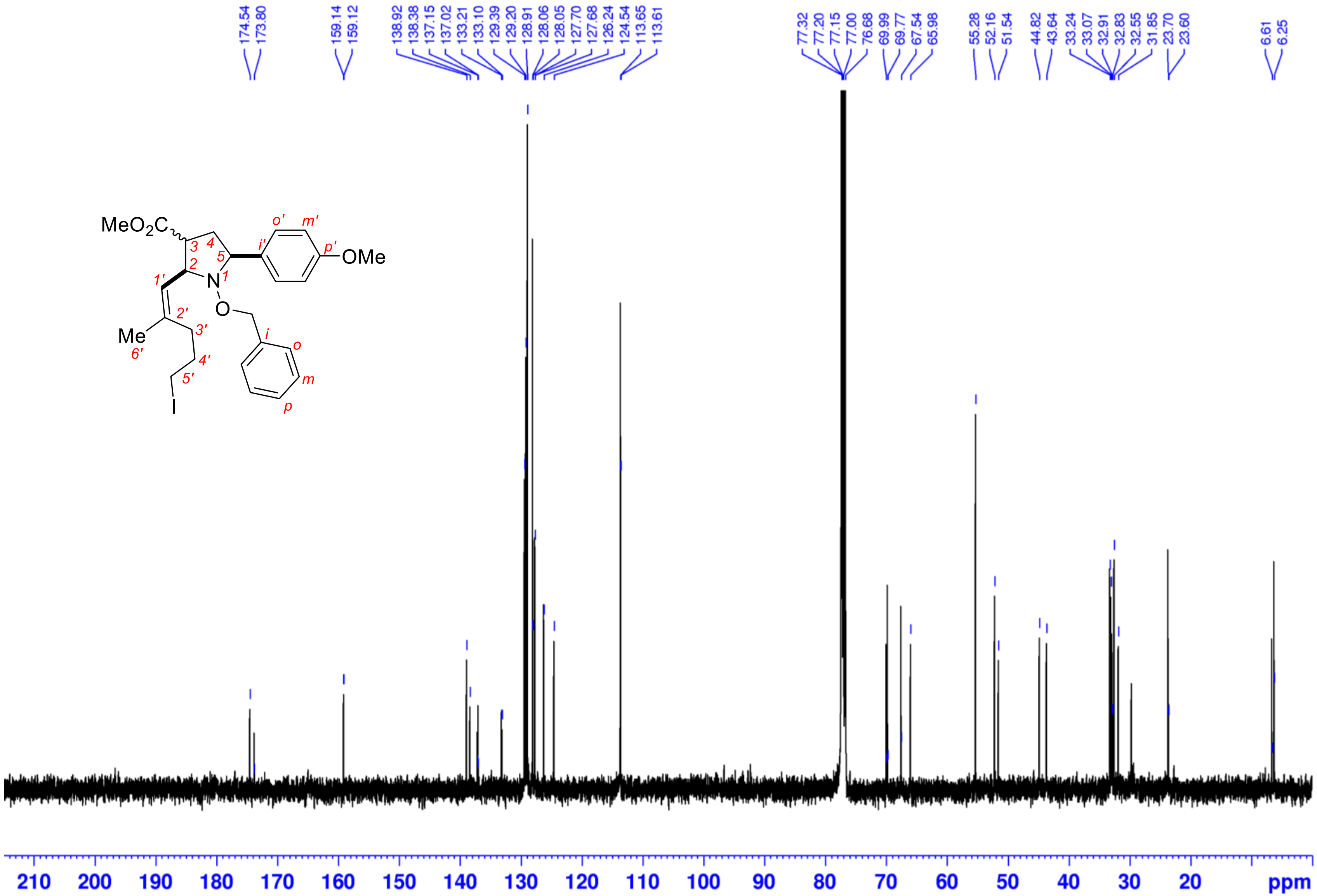


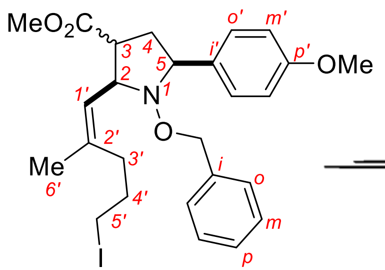

$^{1}$H,$^{13}$C-HMBC NMR spectrum of **14**/**13**, 3:1 ($^{1}$H: 300.1 MHz; $^{13}$C: 75.5 MHz; $CDCl_3$)

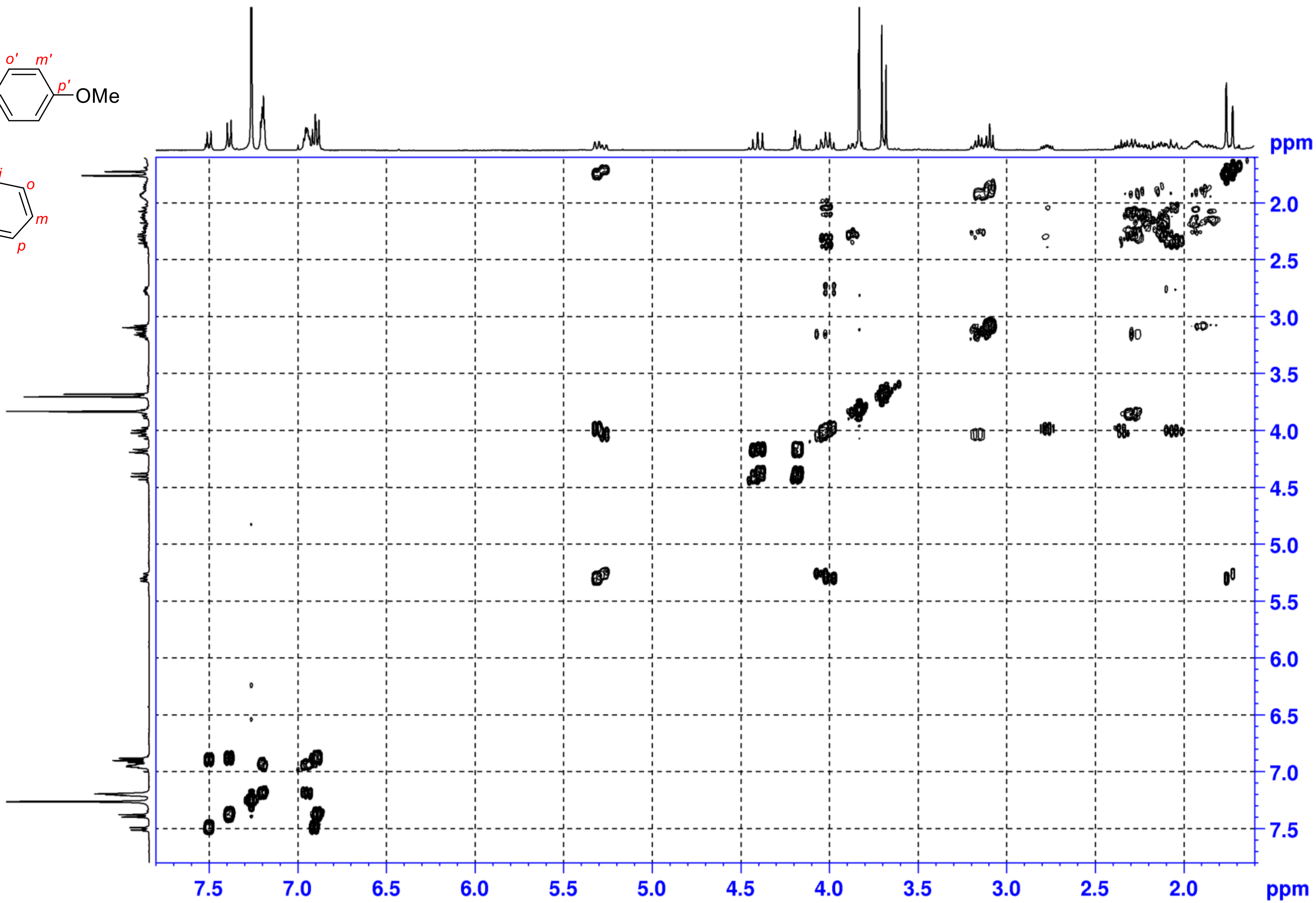



[1]H NMR spectrum of **15**, dr 1.6:1 (400.2 MHz, $CDCl_3$)

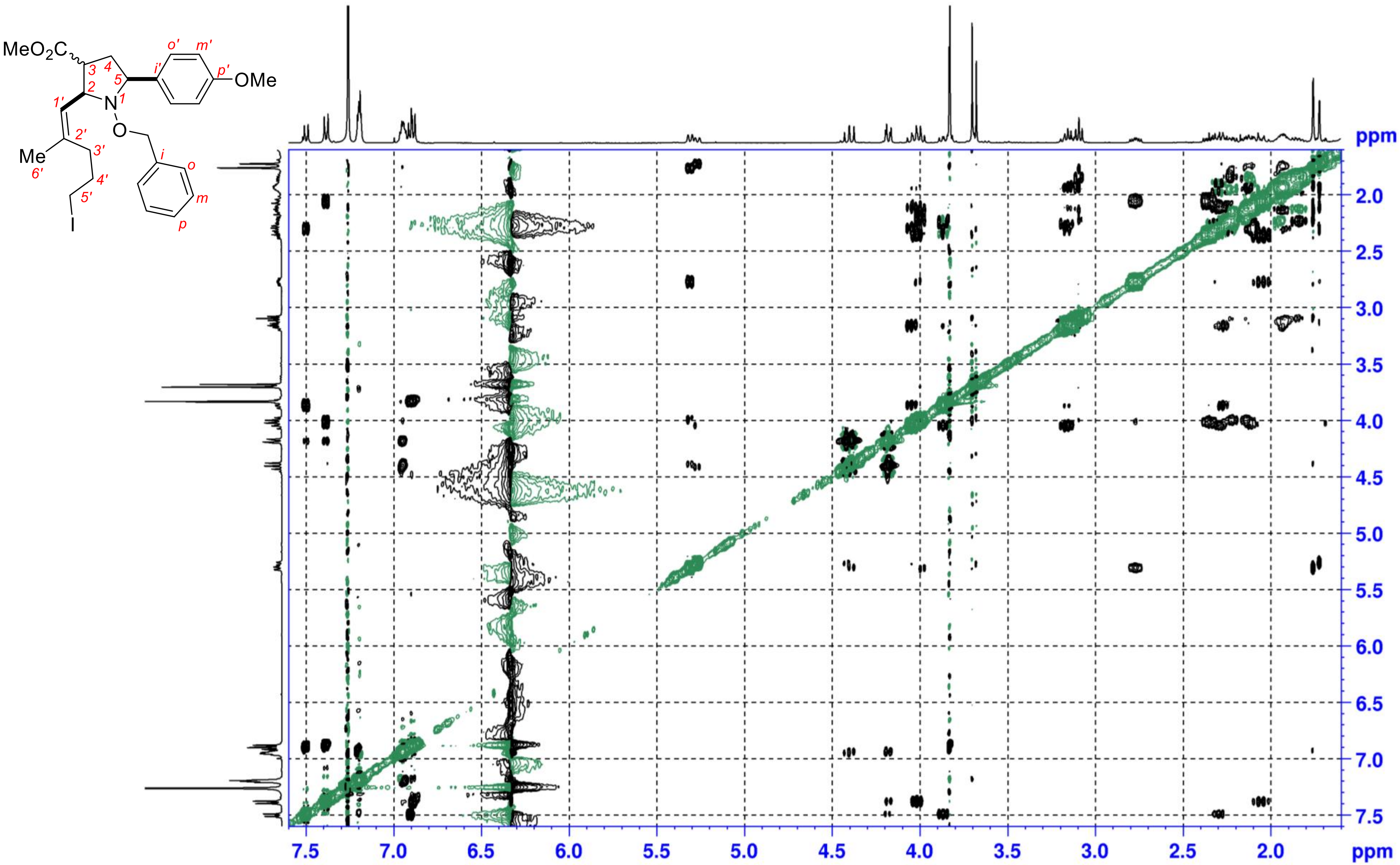



$^{13}$C NMR spectrum of **15**, dr 1.6:1 (100.6 MHz, $CDCl_3$)

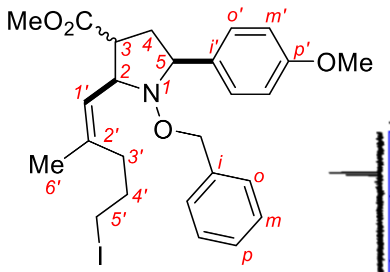


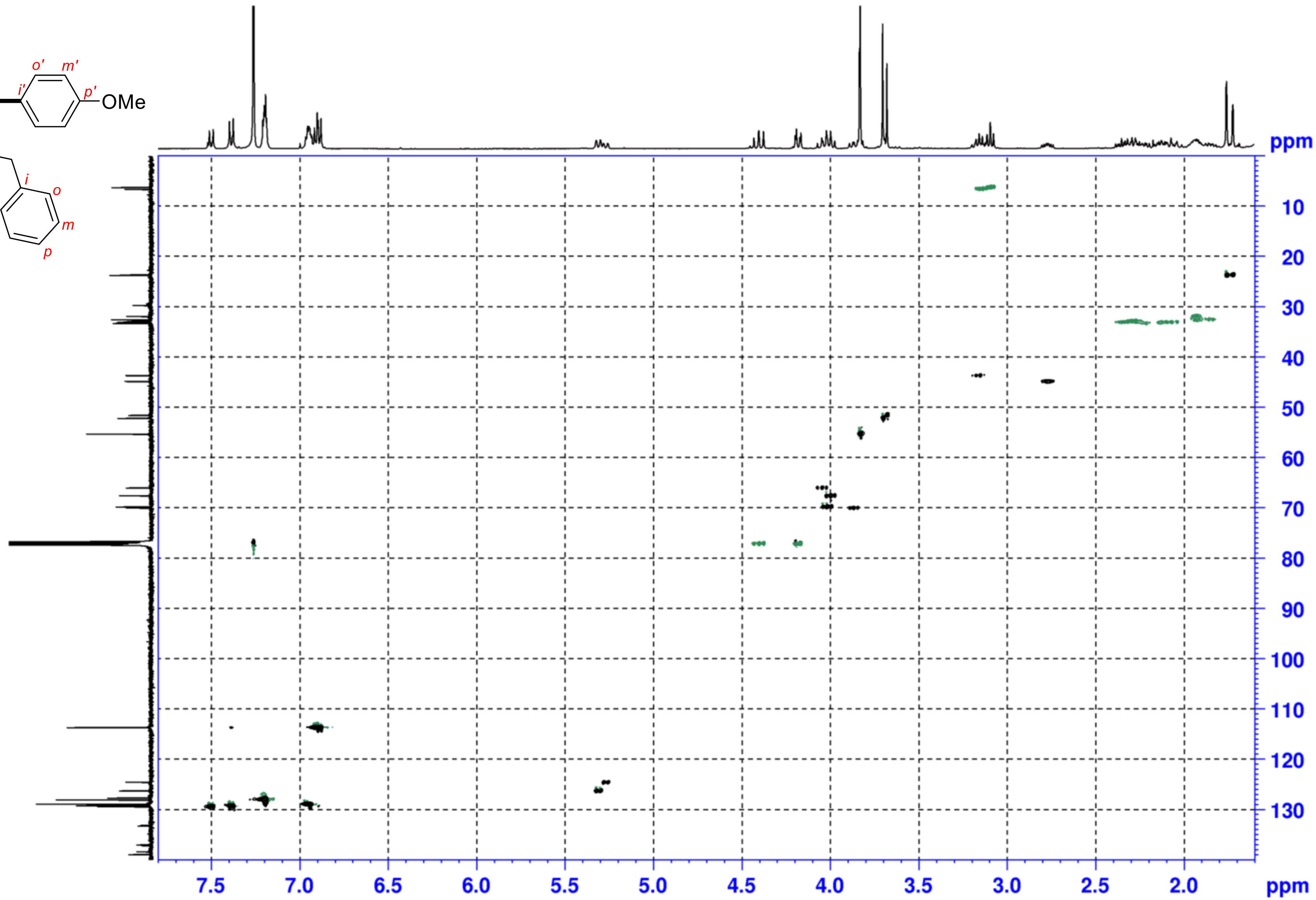




[1]H,[1]H-COSY NMR spectrum of **15**, dr 1.6:1 (400.2 MHz, $CDCl_3$)

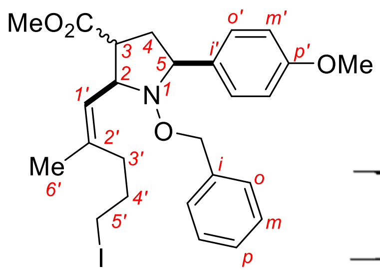


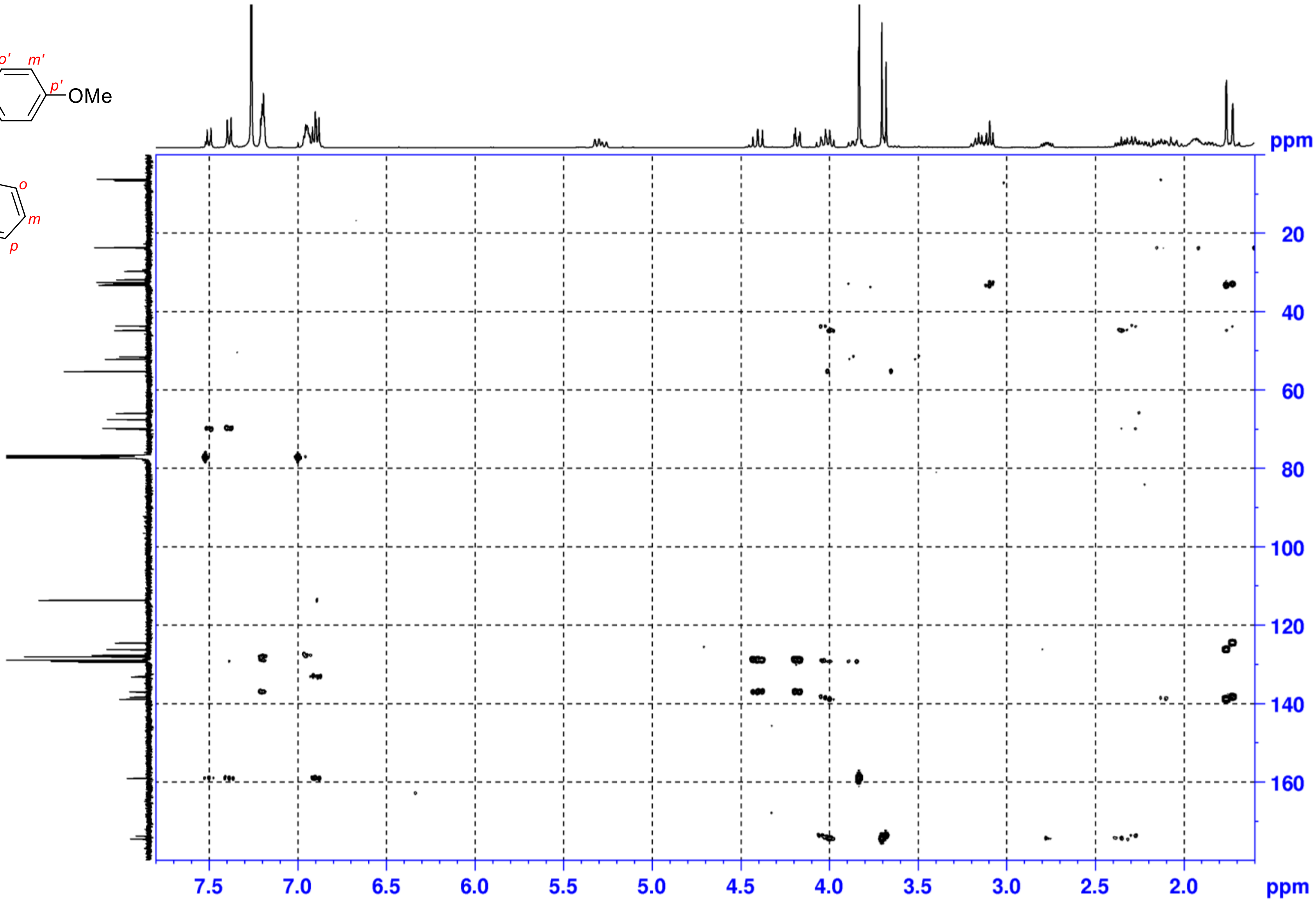

$^{1}H,^{1}H$-NOESY NMR spectrum of **15**, dr 1.6:1 (400.2 MHz, $CDCl_3$)



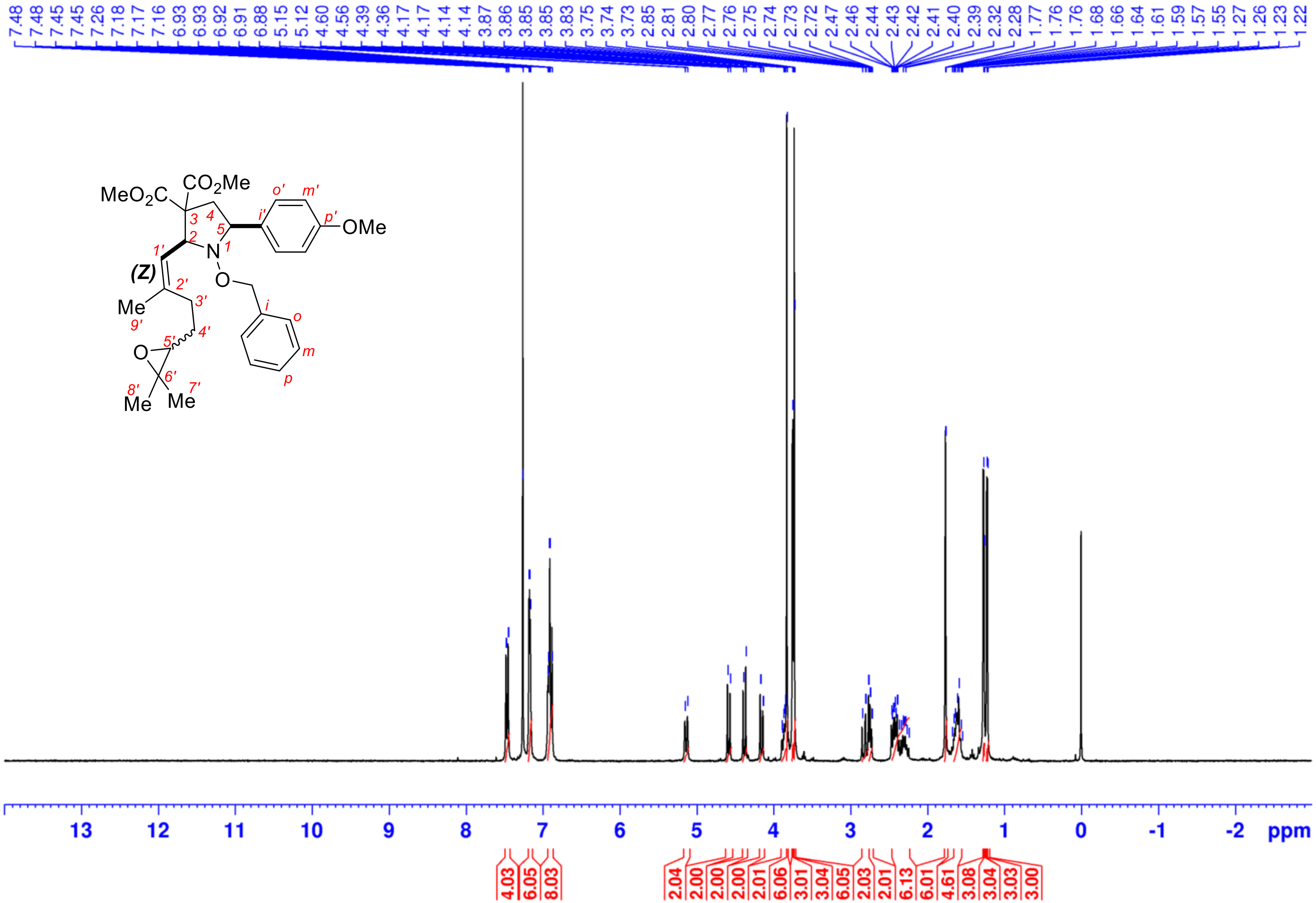




$^1$H,$^{13}$C-edited-HSQC NMR spectrum of **15**, dr 1.6:1 ($^1$H: 400.2 MHz; $^{13}$C: 100.6 MHz; $CDCl_3$)

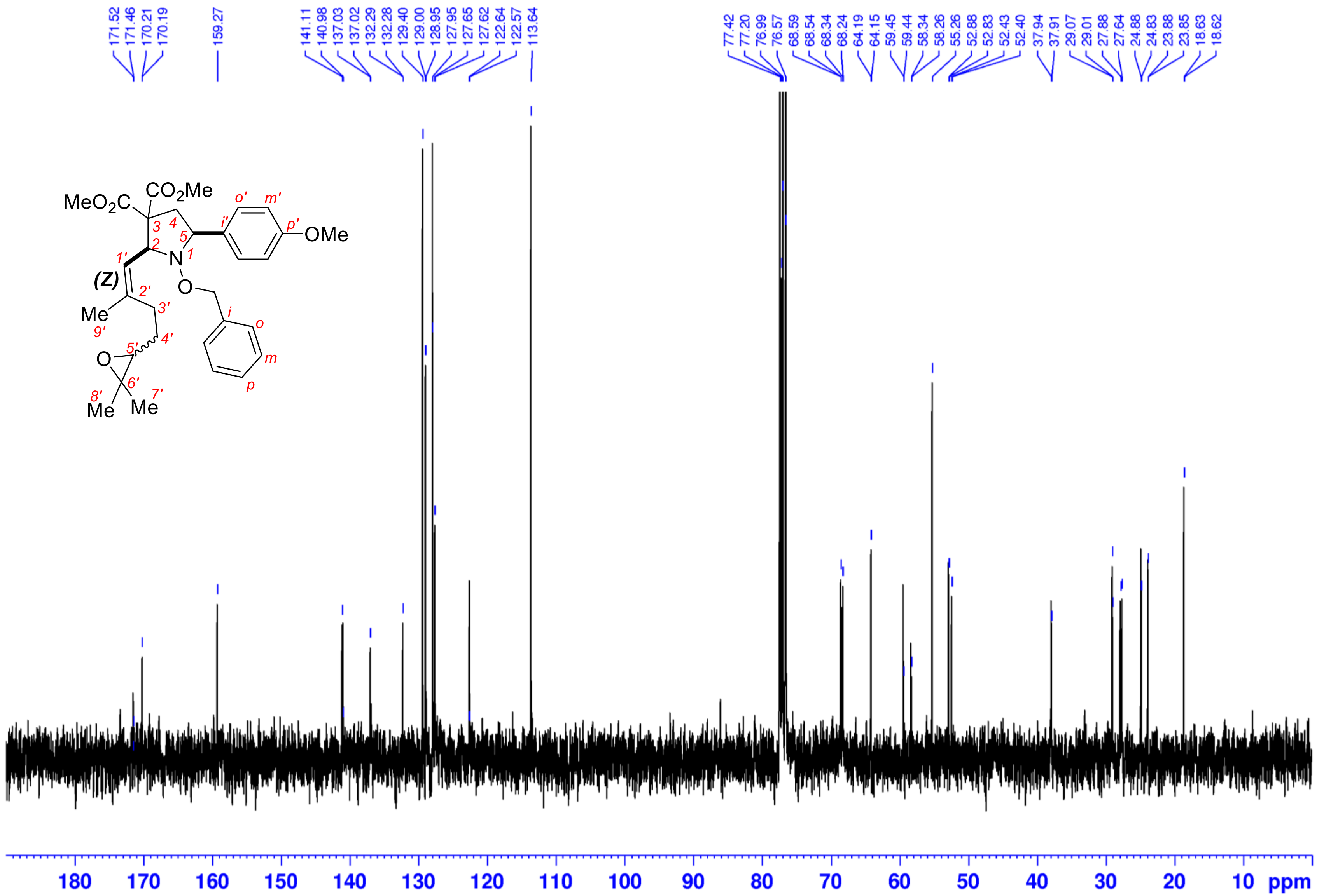


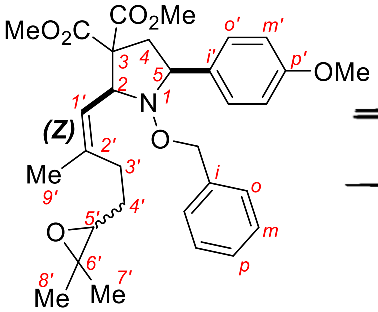

$^{1}$H,$^{13}$C-HMBC NMR spectrum of **15**, dr 1.6:1 ($^{1}$H: 400.2 MHz; $^{13}$C: 100.6 MHz; $CDCl_3$)

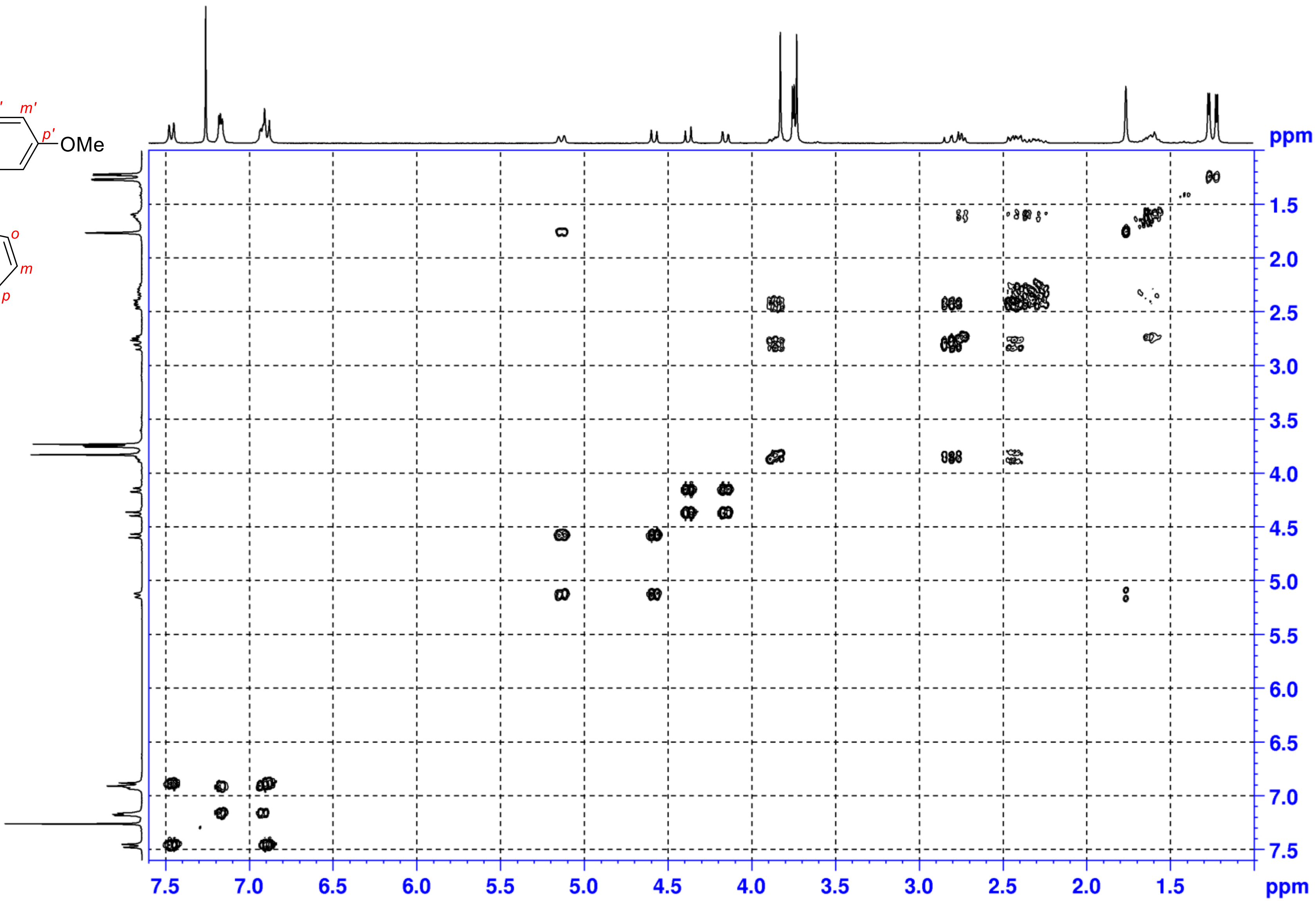


[1]H NMR spectrum of **16**, dr 1:1 (300.1 MHz, $CDCl_3$)

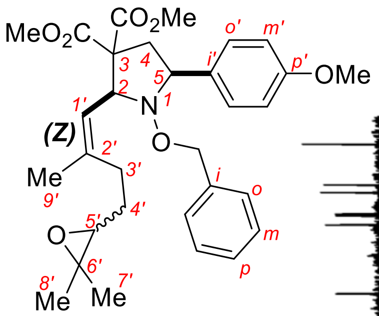


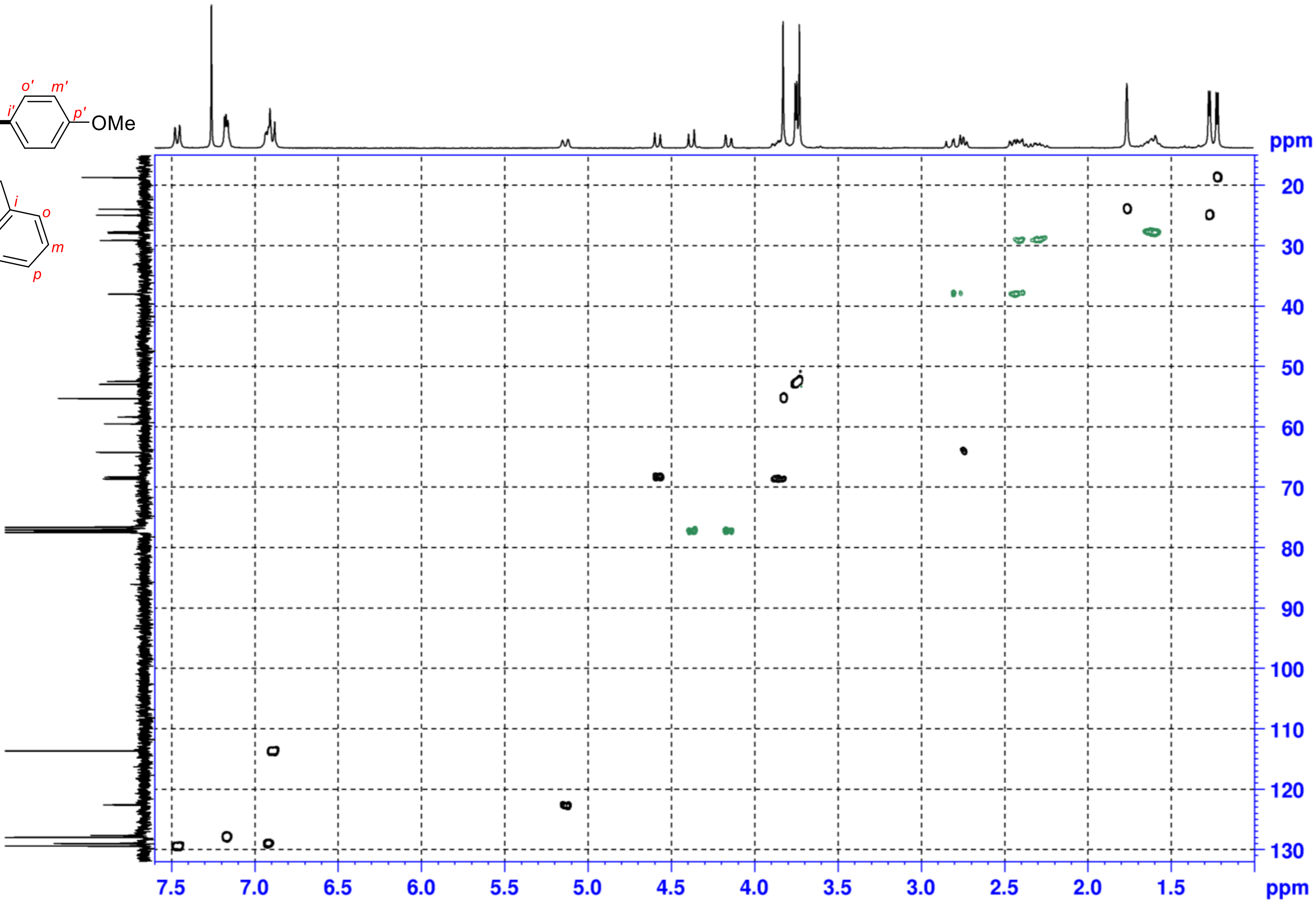

$^{13}$C NMR spectrum of **16**, dr 1:1 (75.5 MHz, $CDCl_3$)



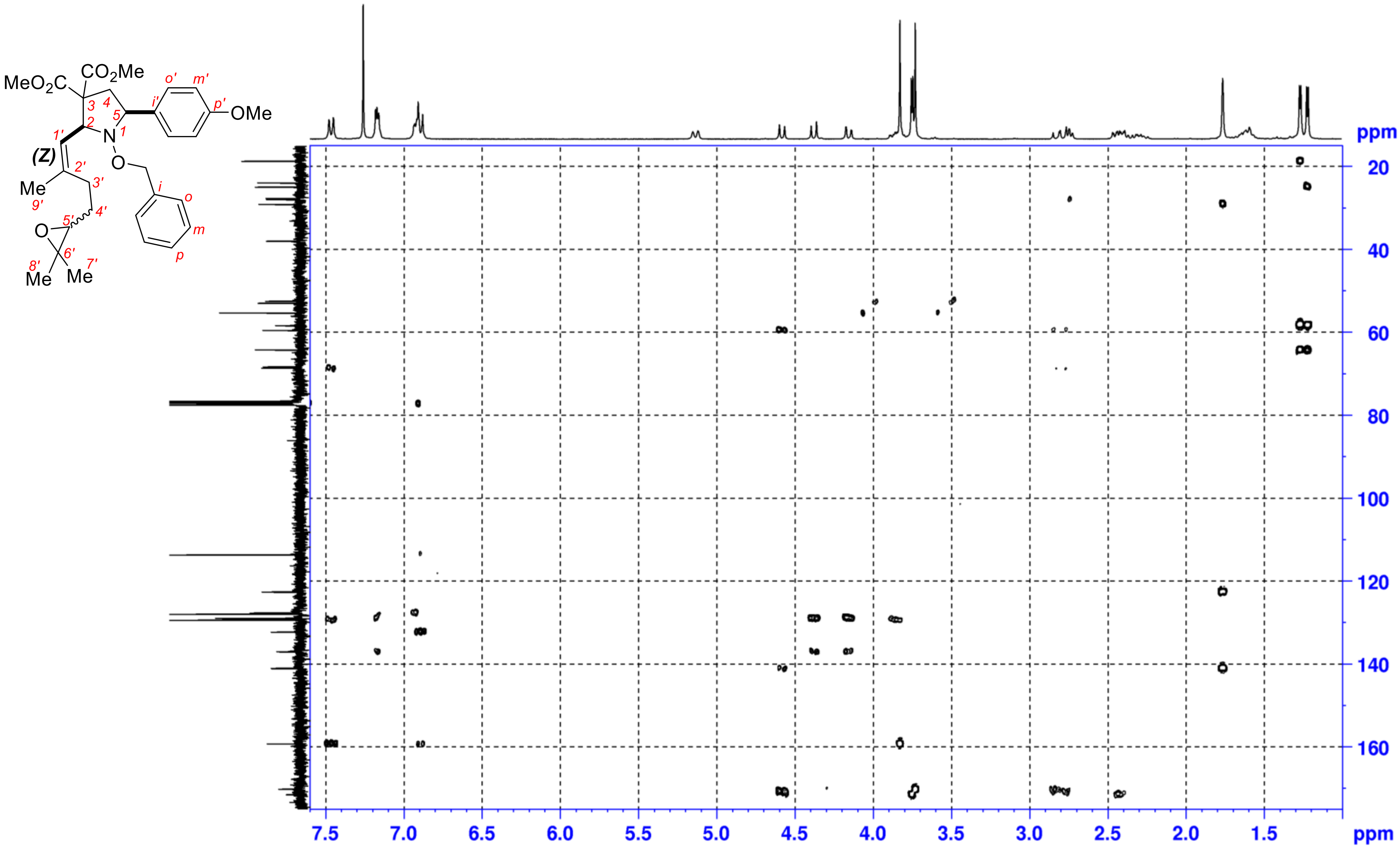




$^1H,^1H$-COSY NMR spectrum of **16**, dr 1:1 (300.1 MHz, $CDCl_3$)

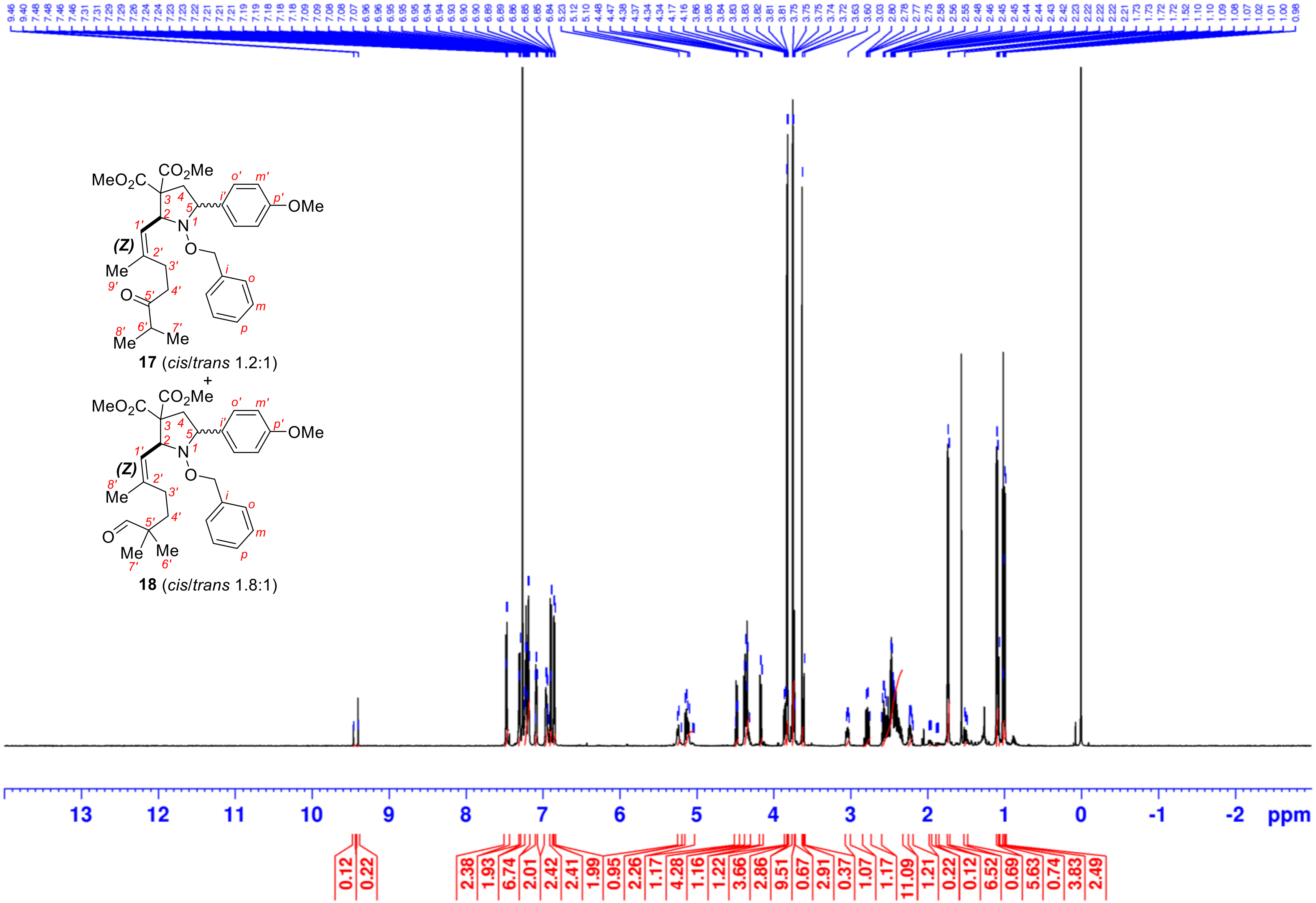


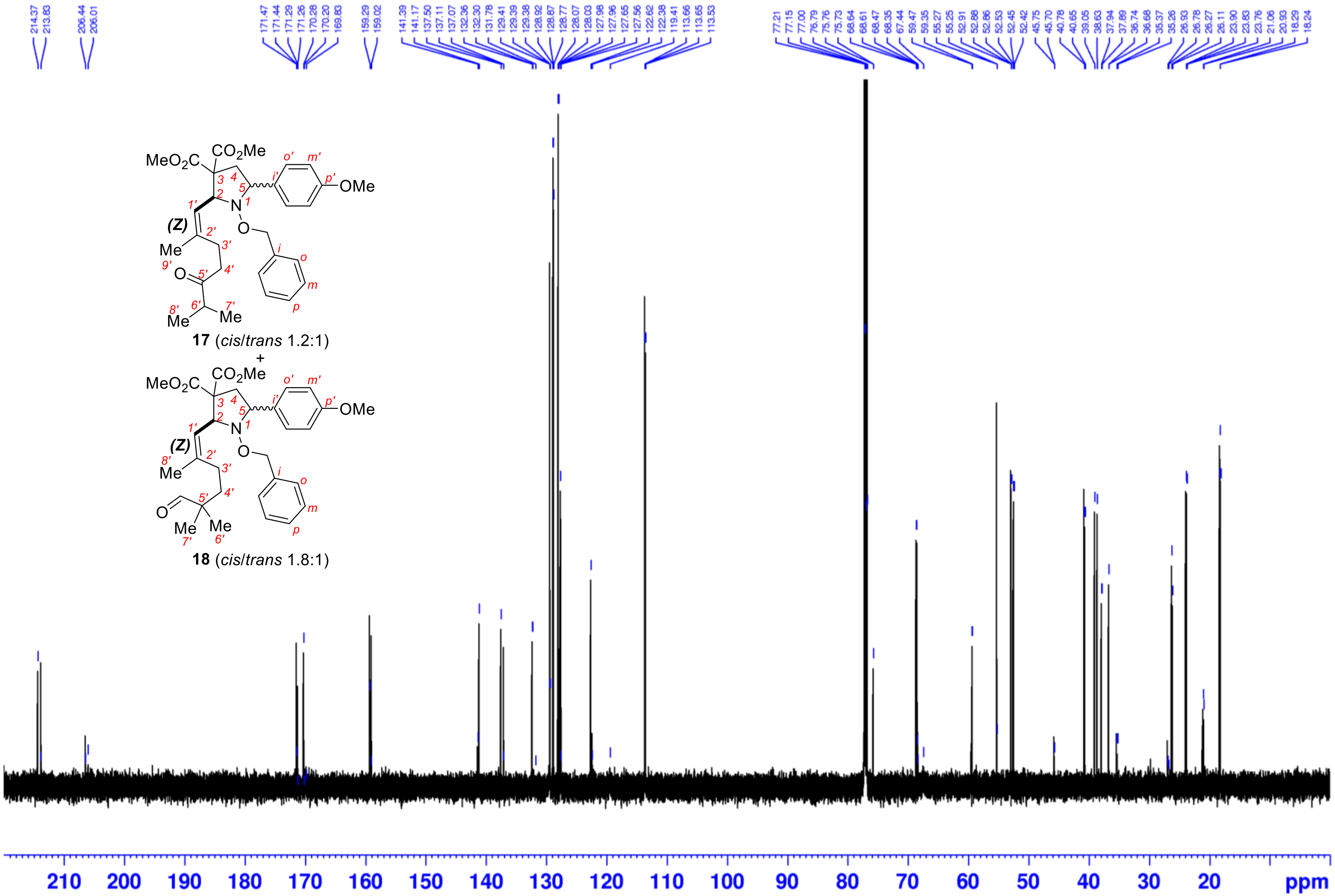

[1]H,[13]C-edited-HSQC NMR spectrum of **16**, dr 1:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)



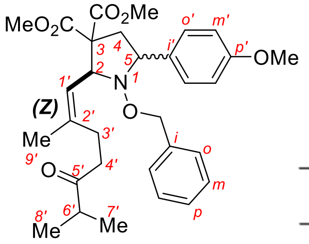

[1]H,[13]C-HMBC NMR spectrum of **16**, dr 1:1 ([1]H: 300.1 MHz; [13]C: 75.5 MHz; $CDCl_3$)




[1]H NMR spectrum of **17**/**18**, 5.4:1 (600.1 MHz, $CDCl_3$)

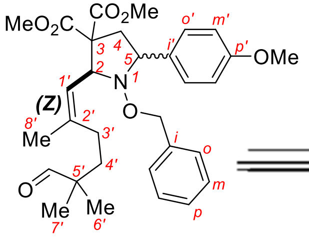


$^{13}$C NMR spectrum of **17**/**18**, 5.4:1 (150.9 MHz, $CDCl_3$)

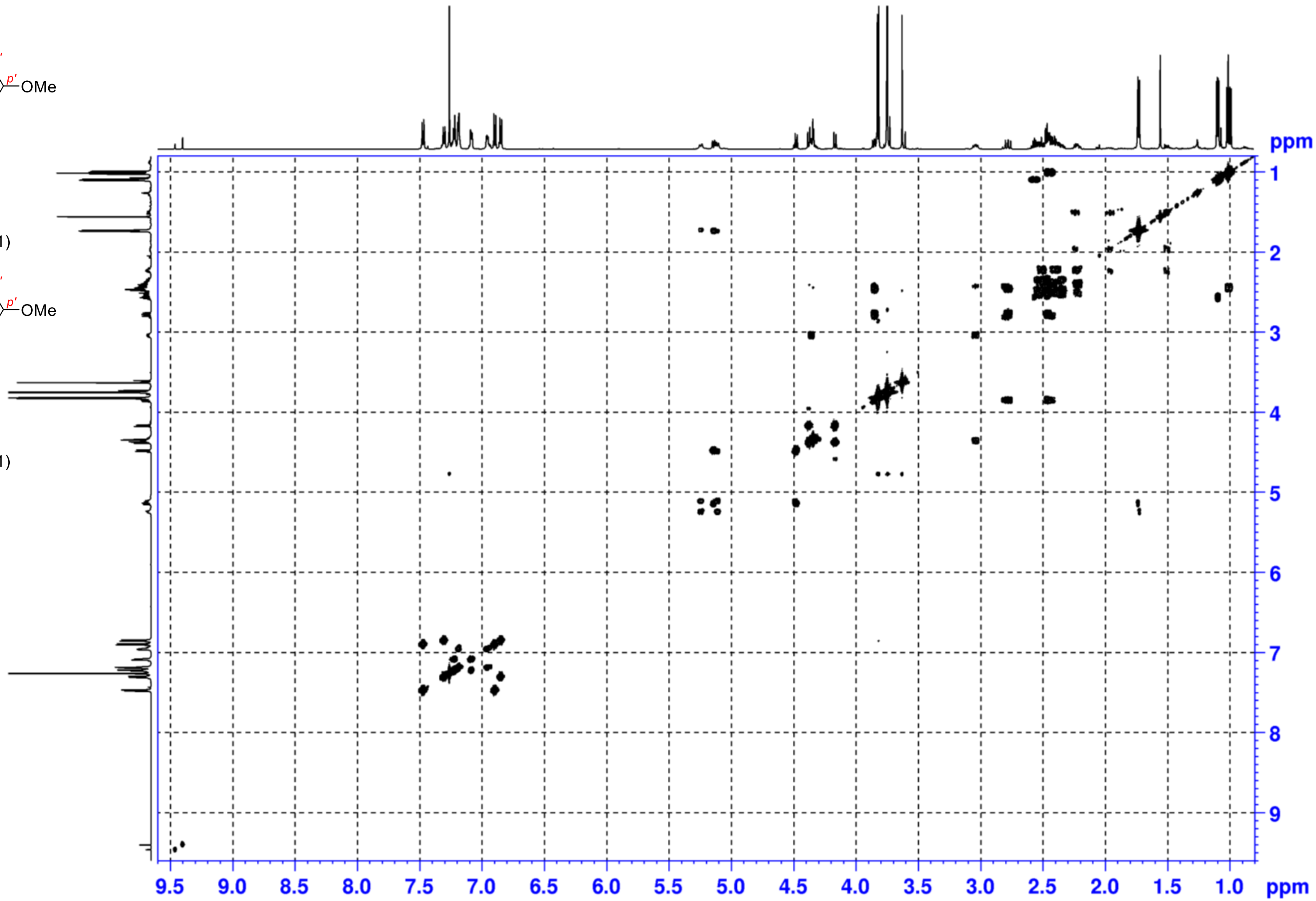



**17** (*cis*/*trans* 1.2:1)

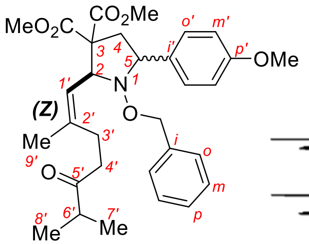
+




**18** (*cis*/*trans* 1.8:1)

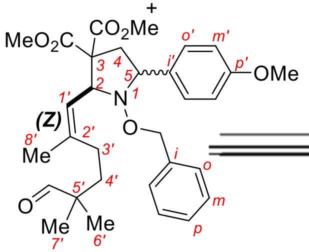



$^1H,^1H$-COSY NMR spectrum of **17**/**18**, 5.4:1 (600.1 MHz, $CDCl_3$)

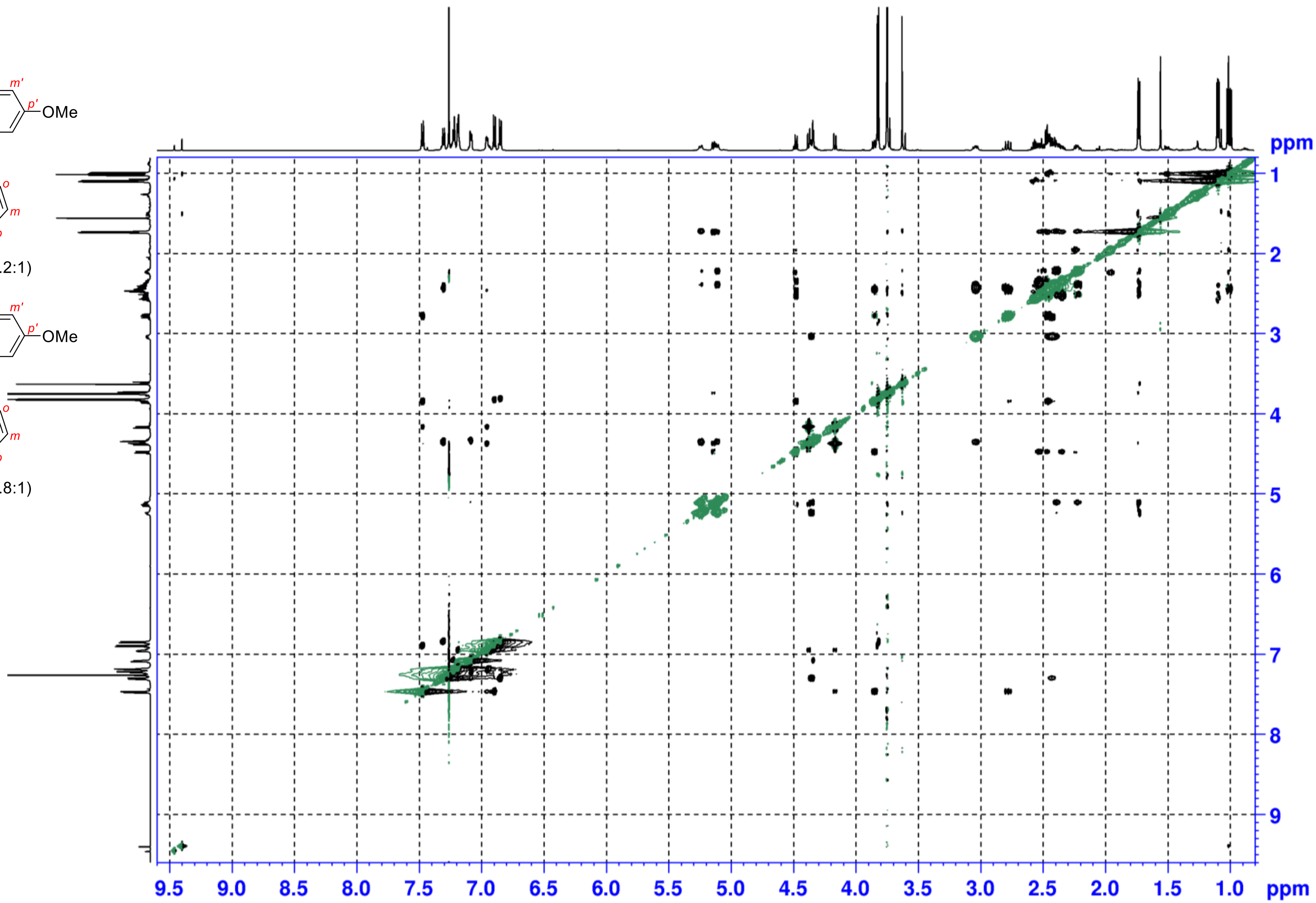



**17** (*cis*/*trans* 1.2:1)

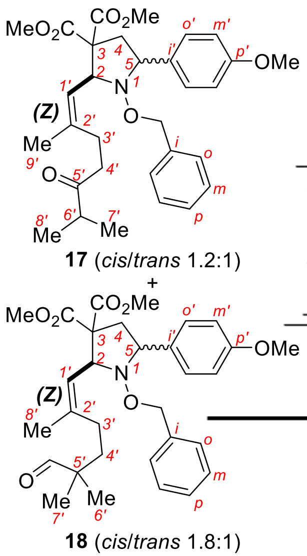
+

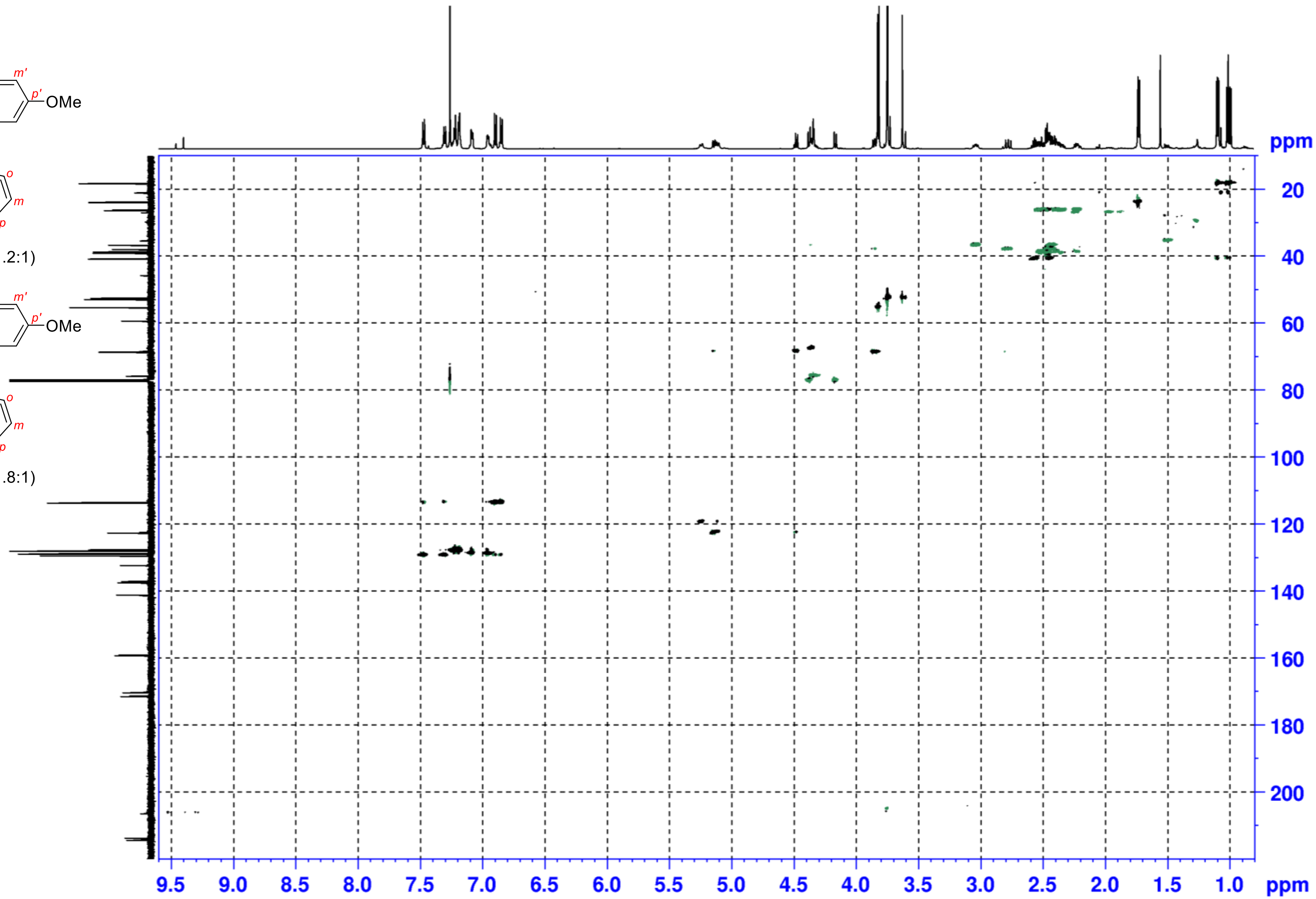



**18** (*cis*/*trans* 1.8:1)

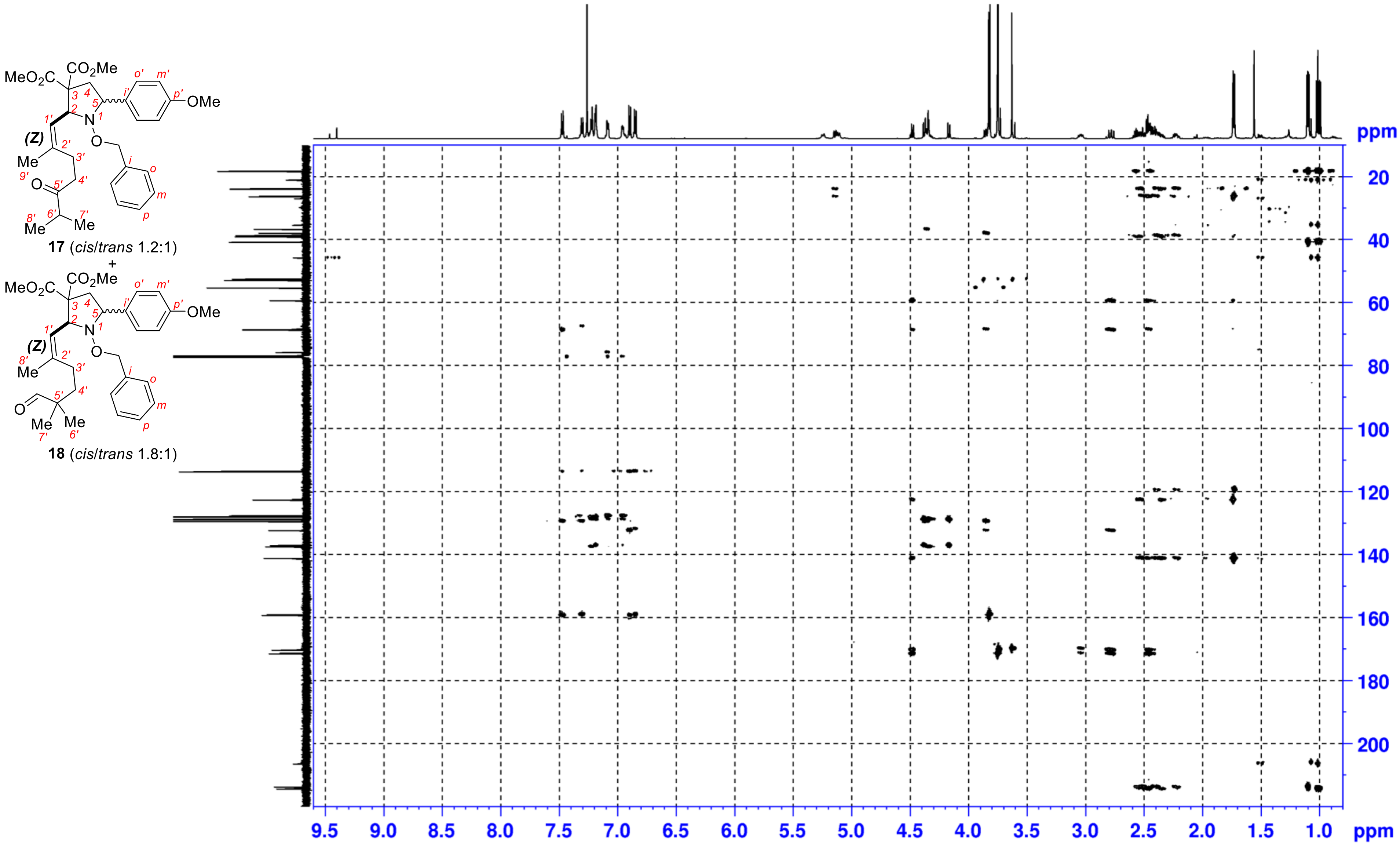



$^1$H,$^1$H-NOESY NMR spectrum of **17**/**18**, 5.4:1 (600.1 MHz, $CDCl_3$)





$^1H,^{13}C$-edited-HSQC NMR spectrum of **17**/**18**, 5.4:1 ($^1H$: 600.1 MHz; $^{13}C$: 150.9 MHz; $CDCl_3$)



$^{1}H,^{13}C$-HMBC NMR spectrum of **17**/**18**, 5.4:1 ($^{1}H$: 600.1 MHz; $^{13}C$: 150.9 MHz; $CDCl_3$)