Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

N- to *C*-Sulfonyl Photoisomerisation of Dihydropyridinones: A Synthetic and Mechanistic Study

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General Information

Reactions involving moisture sensitive reagents were carried out in flame-dried glassware under an inert atmosphere (N_2 or Ar) using standard vacuum line techniques. Anhydrous solvents (CH_2Cl_2, THF and PhMe) were obtained after passing through an alumina column (Mbraun SPS-800). Petrol is defined as petroleum ether 40–60 °C. All other solvents and commercial reagents were used as received without further purification unless otherwise stated.

Room temperature (rt) refers to 20–25 °C. A temperature of 0 °C was obtained using an ice/water bath. Reactions involving heating were performed using DrySyn blocks and a contact thermocouple.

Analytical thin layer chromatography was performed on pre-coated aluminium plates (Kieselgel 60 F254 silica) and visualisation was achieved using ultraviolet light (254 nm) and/or staining with aqueous $KMnO_4$ solution, followed by heating. Column chromatography was performed in glass columns fitted with porosity 3 sintered discs over Kieselgel 60 silica using the solvent system stated. Automated chromatography was performed on a Biotage® Isolera™ 4 running Biotage OS578 with a UV/Vis detector using the method stated and cartridges filled with Kieselgel 60 silica.

Melting points were recorded on an Electrothermal 9100 melting point apparatus, (dec) refers to decomposition.

Optical rotations were measured on a Perkin Elmer Precisely/Model-341 polarimeter operating at the sodium D line with a 100 mm path cell at 20 °C.

HPLC analyses were obtained on a Shimadzu HPLC consisting of a DGU-20A_5 degassing unit, LC-20AT liquid chromatography pump, SIL-20AHT autosampler, CMB-20A communications bus module, SPD-M20A diode array detector and a CTO-20A column oven Separation was achieved using a CHIRALPAK IA column using the method stated, with traces compared with authentic racemic spectra.

Infrared spectra were recorded on a Shimadzu IRAffinity-1 Fourier transform IR spectrophotometer fitted with a Specac Quest ATR accessory (diamond puck). Spectra were recorded of either thin films or solids, with characteristic absorption wavenumbers (ν_{max}) reported in cm^{-1}.

^1H and $^{13}C\{^1H\}$ spectra were acquired on either a Bruker AV400 with a BBFO probe (^1H 400

MHz; $^{13}C\{^{1}H\}$ 101 MHz), a Bruker AVII 400 with a BBFO probe (^{1}H 400 MHz; $^{13}C\{^{1}H\}$ 101 MHz), or a Bruker AVIII-HD 500 with a SmartProbe BBFO+ probe (^{1}H 500 MHz, $^{13}C\{^{1}H\}$ 126 MHz) in the deuterated solvent stated. All chemical shifts are quoted in parts per million (ppm) relative to the residual solvent peak. All coupling constants, *J*, are quoted in Hz. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and multiples thereof. The abbreviation Ar denotes aromatic and br denotes broad.

Mass spectrometry (*m/z*) data were acquired by either electrospray ionisation (ESI) or nanospray ionisation (NSI) at the EPSRC UK National Mass Spectrometry Facility at Swansea University.

EPR spectra were obtained at 9.5 GHz with 100 kHz modulation employing a Bruker EMX 10/12 spectrometer fitted with a rectangular ER4122 SP resonant cavity. The compound (10 to 15 mg) in tert-butylbenzene (0.5 cm^3) was prepared and sonicated. An aliquot (0.2 cm^3) was placed in a 4 mm o.d. quartz tube, de-aerated by bubbling nitrogen for 15 min. Photolysis in the resonant cavity was by unfiltered light from a 500 W super pressure mercury arc lamp. Hfs were assigned with the aid of computer simulations using the Bruker SimFonia and NIEHS Winsim2002 software packages. EPR signals were digitally filtered using the Bruker WinEPR software. The EPR spectra were recorded with 4.0 mW power, 1.2 G pp modulation intensity and gain of 2 x 10^6 and 70 scans were accumulated.

UV Photoisomerisation Equipment and Setup

A UV light box was prepared in-house containing ten 365 nm black UV lamps with the chamber designed to fit over a standard stirring hotplate. A round-bottom flask placed on a cork ring or sealed standing tubes can be used for the reaction. A standard fan system was positioned at the top of the chamber to cool the reaction chamber during use, with the internal temperature measured as 30 °C.

CAUTION! Do not look directly at UV light while in opperation.

Fig. S1 (Left) Open UV-box showing ten 365 nm black UV lamps. (Right) Closed UV-box as used for photoisomerisation reaction with a standard fan placed at the top of the chamber for cooling.

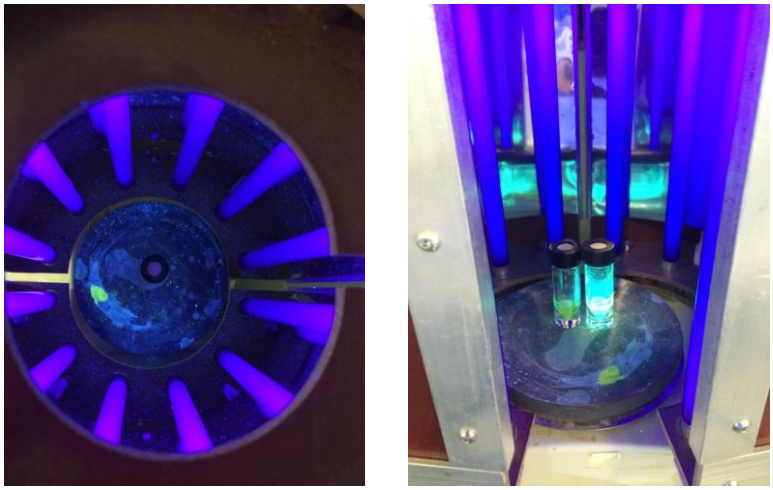
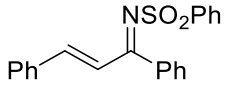


Fig. S2 (Left) View down into the UV chamber while active. (Right) Side view into the UV chamber while active.

Starting Material Synthesis

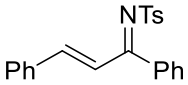
α,β-Unsaturated Ketimines

_N_-((2_E_)-1,3-Diphenylallylidene)benzenesulfonamide (S1)



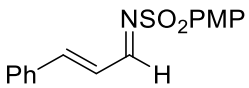
(*E*)-Chalcone (4.16 g, 20.0 mmol) was dissolved in CH_2Cl_2 (40 mL) before benzenesulfonamide (3.14 g, 20.0 mmol), Et_3N (5.6 mL, 40.0 mmol) and $TiCl_4$ (2.2 mL, 20.0 mmol) were added. The reaction was heated at reflux overnight before being concentrated under reduced pressure. The crude material was purified by trituration (Et_2O) to give the title compound (5.46 g, 79%) as a white solid. mp 123–125 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 7.09 (1H, d, *J* 16.2, C(3)*H*), 7.38–7.49 (5H, m, Ar*H*), 7.48–7.75 (8H, m, Ar*H*), 8.05–8.06 (3H, m, Ar*H*). Data in accordance with the literature.[1]

_N_-((2_E_)-1,3-Diphenylallylidene)-4-methylbenzenesulfonamide (S2)



(*E*)-Chalcone (4.16 g, 20.0 mmol) was dissolved in CH_2Cl_2 (40 mL) before 4-toluenesulfonamide (3.42 g, 20.0 mmol), Et_3N (5.6 mL, 40.0 mmol) and $TiCl_4$ (2.2 mL, 20.0 mmol) were added. The reaction was heated at reflux overnight before being concentrated under reduced pressure. The crude material was purified by trituration (Et_2O) to give the title compound (6.54 g, 90%) as a yellow solid. mp 146–148 °C {Lit.[2] 116–120 °C}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 2.45 (3H, s, ArC*H*$_3$), 7.10 (1H, d, *J* 16.0, C(3)*H*), 7.34 (2H, d, *J* 8.0, Ar*H*), 7.39–7.53 (5H, m, Ar*H*), 7.53–7.72 (5H, m, Ar*H*), 7.89–8.02 (2H, m, Ar*H*), 8.12 (1H, s, Ar*H*). Data in accordance with the literature.[2]

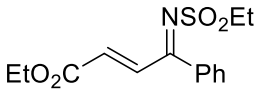
4-Methoxy-_N_-((2_E_)-3-phenylallylidene)benzenesulfonamide (S3)



A solution of 4-toluenesulfonamide (0.66 g, 5.0 mmol) and *trans*-cinnamaldehyde (0.68 g, 5.0 mmol) in toluene (5 mL) was heated at reflux for 16 h using Dean-Stark apparatus. The reaction was cooled to rt before Et_2O was added. The resulting precipitate was filtered to give the title

compound (1.26 g, 88%) as a white solid. mp 115–116 °C {Lit.[3] 125-190 °C}; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.88 (3H, s, OC*H*$_3$), 6.96–7.02 (3H, m, SO_2ArC(3,5)*H* and C(2)*H*), 7.41–7.49 (4H, m, C(3)*H* and Ar*H*), 7.53–7.56 (2H, m, Ar*H*), 7.90 (2H, d, *J* 8.9, SO_2ArC(2,6)*H*), 8.76 (1H, d, *J* 9.4, C(1)*H*). Data in accordance with the literature.[3]

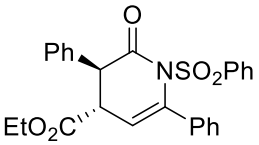
Ethyl (2*E*)-4-((ethylsulfonyl)imino)-4-phenylbut-2-enoate (S4)



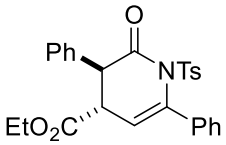
Ethyl (*E*)-4-oxo-4-phenylbut-2-enoate (531 mg, 2.6 mmol) and ethanesulfonamide (284 mg, 2.6 mmo) were dissolved in CH_2Cl_2 (13 mL). The solution was cooled to 0 °C before Et_3N (0.73 mL, 5.2 mmol) was added followed by dropwise addition of $TiCl_4$ (0.28 mL, 2.6 mmol), resulting in a deep red solution that was allowed to warm slowly to rt overnight. The reaction was quenched with H_2O (15 mL), the layers were separated and the aqueous extracted with EtOAc (×2). The combined organics were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by Biotage® Isolera™ 4 [SNAP KP-Sil 25 g, 75 mLmin^{-1}, hexane/EtOAc (95:5 1 CV, 95:5 to 65:35 10 CV, 65:35 3 CV)] to give the title compound (430 mg, 56%) as a beige solid. mp 60–61 °C; ν_{max} (ATR, cm^{-1}) 1722, 1547, 1443, 1300, 1285, 1265, 1240, 1177, 1130; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 1.31 (3H, t, *J* 7.0, OCH_2CH_3), 1.51 (3H, t, *J* 6.9, $SO_2CH_2CH_3$), 3.27–3.36 (2H, m, SO_2CH_2), 4.26 (2H, q, *J* 7.0, OCH_2), 6.24 (1H, d, *J* 16.2, C(2)*H*), 7.42–7.49 (2H, m, ArC(3,5)*H*), 7.55–7.62 (1H, m, ArC(4)*H*), 7.73–7.75 (2H, m, ArC(2,6)*H*), 8.14 (1H, d, *J* 16.2, C(3)*H*); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ_C: 8.2, 14.2, 49.5, 61.7, 128.8, 130.1, 133.4, 133.4, 135.9, 136.4, 164.7, 175.6; HRMS (NSI$^+$) $C_{14}H_{18}NO_4S$ $[M+H]^+$ found 296.0955, required 296.0951 (+1.3 ppm).

N-Sulfonyl Dihydropyridinones

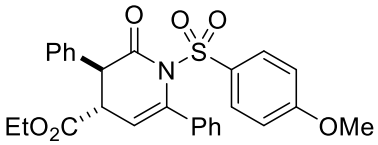
The following (*rac*)-*anti*-dihydropyridinone starting materials were synthesised according to our previously reported procedures.



6, *Ref:* 4



18, *Ref:* 4



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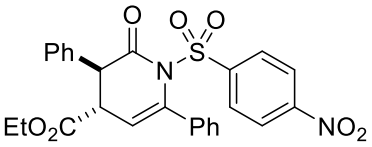

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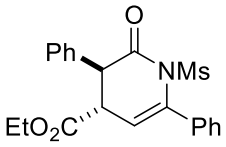

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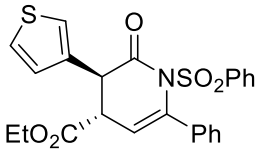

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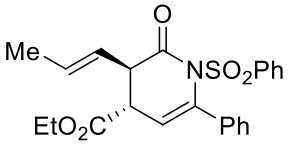

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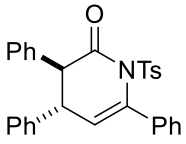
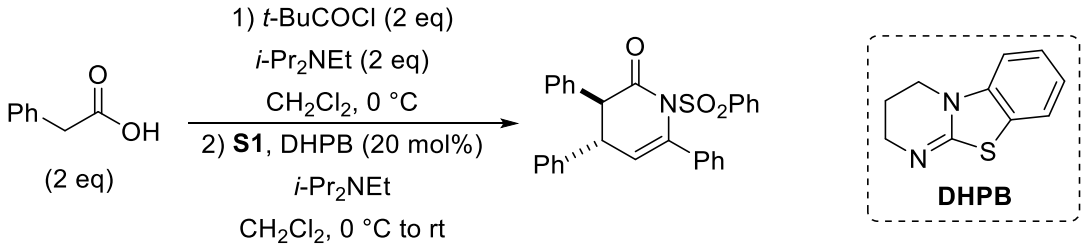


4, *Ref:* 2

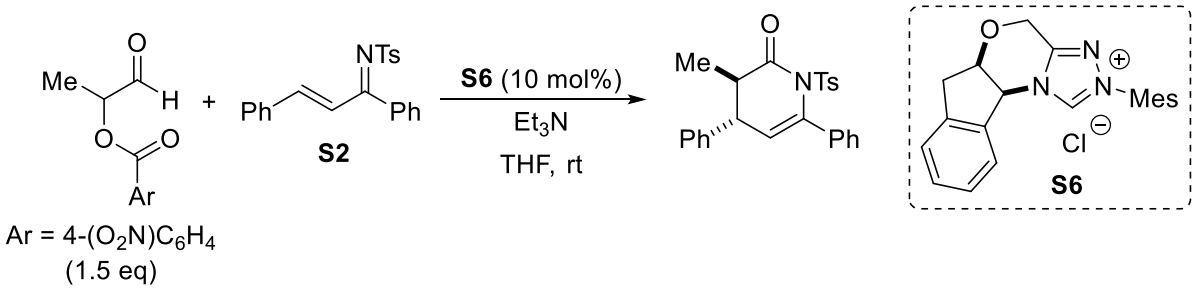
(*rac*)-*anti*-3,4,6-Triphenyl-1-(phenylsulfonyl)-3,4-dihydropyridin-2(1H)-one (19)



Phenylacetic acid (0.55 g, 4.0 mmol) was suspended in CH_2Cl_2 (10 mL) before *i*-Pr_2NEt (0.70 mL, 4.0 mmol) was added and the solution cooled to 0 °C. Pivaloyl chloride (0.50 mL, 4.0 mmol) was added and the reaction stirred for 30 minutes. DHPB (76.1 mg, 20 mol%) was added followed by a solution of ketimine **S1** (0.70 mg, 2.0 mmol) and *i*-Pr_2NEt (0.35 mL, 2.0 mmol) in CH_2Cl_2 (20 mL). After 1 h the reaction was complete by TLC analysis and was quenched with 0.1 M aq. HCl (~20 mL/mmol acid). The layers were separated and the aqueous extracted with CH_2Cl_2 (×2). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure (water bath < 30 °C). The crude product (94:6 dr) was purified by column chromatography (CH_2Cl_2) followed by recrystallisation (Et_2O) to give the title compound (0.42 g, 46%, 94:6 dr) as a white solid. mp 182–184 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ_H: 3.92 (1H, d, *J* 10.7, C(3)*H*), 4.04 (1H, dd, *J* 10.7, 4.2, C(4)*H*), 6.04 (1H, d, *J* 4.2,

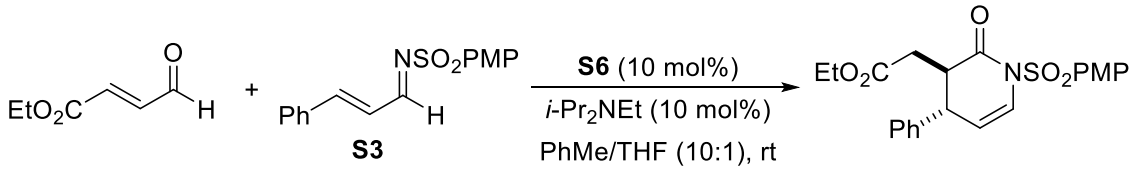
C(5)*H*), 6.80–6.82 (2H, m, C(4)Ar*C*(2,6)*H*), 7.03–7.05 (2H, m, C(3)Ar*C*(2,6)*H*), 7.13–7.20 (6H, m, Ar*H*), 7.36–7.45 (5H, m, Ar*H*), 7.47–7.52 (2H, m, NSO_2Ar*C*(3,5)*H*), 7.63–7.67 (1H, m, NSO_2Ar*C*(4)*H*), 7.96–7.99 (2H, m, NSO_2Ar*C*(2,6)*H*); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ_C: 45.3 (*C*(4)), 59.1 (*C*(3)), 123.1 (*C*(5)), 126.2 (Ar*C*), 127.3 (Ar*C*), 127.5 (Ar*C*), 127.9 (C(3)Ar*C*(2)), 128.5 (Ar*C*), 128.6 (Ar*C*), 128.7 (NSO_2ArC(2)), 128.8 (Ar*C*), 128.9 (C(4)Ar*C*(2)), 129.5 (NSO_2Ar*C*(2)), 134.0 (NSO_2Ar*C*(4)), 136.4 (C(3)Ar*C*(1)), 137.1 (C(6)Ar*C*(1)), 139.4 (NSO_2Ar*C*(1)), 140.0 (C(4)Ar*C*(1)), 140.2 (*C*(6)), 173.2 (*C*(2)O); HRMS (ESI^+) $C_{29}H_{23}NO_3SNa$ $[M+Na]^+$ found 488.1282, requires 488.l1291 (–1.8 ppm).

(*rac*)-*anti*-3-Methyl-4,6-diphenyl-1-tosyl-3,4-dihydropyridin-2(1*H*)-one (S5)



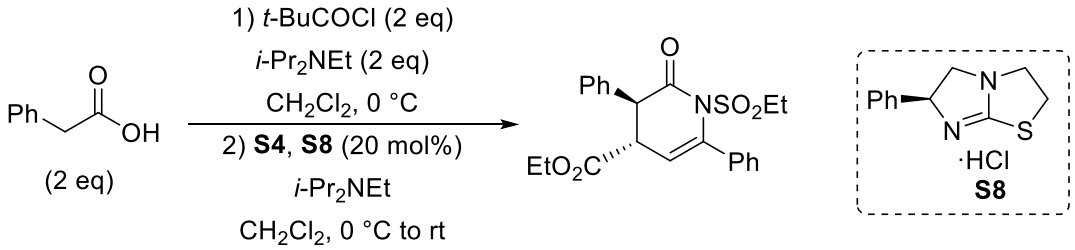
Following the procedure by Smith,[5] 1-oxopropan-2-yl 4-((λ1-oxidanyl)diazenyl)benzoate[5] (134.0 mg, 0.6 mmol), ketimine **S2** (144.6 mg, 0.4 mmol), and NHC precatalyst **S6** (14.7 mg, 10 mmol) were dissolved in anhydrous THF (8 ml) in a sealed vial containing 4 Å molecular sieves. Et_3N (84 µl, 0.6 mmol) was added and the reaction mixture was stirred at rt until complete by TLC analysis. The mixture was diluted with EtOAc and washed successively with 1 M aq. HCl, saturated aq. $NaHCO_3$, and brine. The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure (water bath < 30 °C) to give the crude product in 74:26 dr. Purification by column chromatography (Petrol/Et_2O, 95:5), gave the title compound (146 mg, 87%, 74:26 dr) as a white solid. mp 148–150 °C; ^1H NMR (400 MHz, $CDCl_3$) δ_H: 0.94 (3H, d, *J* 6.9, C*H*$_3$), 2.45 (3H, s, SO_2ArC*H*$_3$), 2.66 (1H, dq, *J* 12.1, 6.9, C(3)*H*), 3.45 (1H, dd, *J* 12.0, 3.7, C(4)*H*), 5.91 (1H, d, *J* 3.7, C(5)*H*), 7.16–7.20 (2H, m, Ar*H*), 7.23–7.43 (7H, m, Ar*H*), 7.83 (2H, m, Ar*H*); Data in accordance with the literature.[6]

(*rac*)-Ethyl 2-(*anti*-1-((4-methoxyphenyl)sulfonyl)-2-oxo-4-phenyl-1,2,3,4-tetrahydropyridin-3-yl)acetate (17)



Following the procedure outlined by Bode.,[7] ethyl *trans*-4-oxo-2-butenoate (66 µl, 0.55 mmol), ketimine **S3** (150.7 mg, 0.5 mmol), and NHC precatalyst **S6** (16.6 mg, 0.05 mmol) were dissolved in toluene/THF (10 mL : 1 mL) in a sealed vial containing 4 Å molecular sieves. *i*-Pr_2NEt (8.6 µl, 0.05 mmol) was added and the reaction mixture was stirred at rt until complete by TLC analysis. The mixture was diluted with EtOAc and washed successively with 1 M aq. HCl, saturated aq. $NaHCO_3$ and brine. The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure (water bath < 30 °C) to give the crude product in 85:15 dr. Purification by column chromatography (Petrol/Et_2O, 95:5), gave the title compound (49.9 mg, 25%, 85:15 dr) as a white solid. mp 118–119 °C {Lit.[7] 111–113 °C}; ^{1}H NMR (400 MHz, $CDCl_3$) *major diastereoisomer* δ_H: 1.21 (3H, t, *J* 7.0, CH_2CH_3), 1.94 (1H, dd, *J* 17.3, 7.5, C(3)HCH^AH^B), 2.57 (1H, dd, *J* 17.3, 6.0, C(3)HCH^AH^B), 3.51-3.56 (1H, m, C(3)*H*), 3.65 (1H, t, *J* 6.8, C(4)*H*), 3.92 (3H, s, OCH_3), 4.07–4.17 (2H, m, CH_2CH_3), 5.60 (1H, dd, *J* 8.0, 6.5, C(5)*H*), 6.56–6.60 (2H, m, SO_2ArC(3,5)*H*), 6.99–7.07 (4H, m, C(4)Ar(2,4,6)*H* and C(6)*H*), 7.12–7.17 (2H, m, C(4)ArC(3,5)*H*), 8.02–8.06 (2H, m, SO_2ArC(2,6)*H*). Data in accordance with literature.[7]

Ethyl (3*S*,4*S*)-1-(ethylsulfonyl)-2-oxo-3,6-diphenyl-1,2,3,4-tetrahydropyridine-4-carboxylate (S7)



Phenylacetic acid (82 mg, 0.6 mmol) was suspended in CH_2Cl_2 (1.5 mL) before *i*-Pr_2NEt (105 µL, 0.6 mmol) was added and the solution cooled to 0 °C. Pivaloyl chloride (73 µL, 0.6 mmol) was added and the reaction stirred for 20 min. (–)-Tetramisole·HCl **S8** (14 mg, 0.06 mmol) was added followed by a solution of ketimine **S4** (89 mg, 0.3 mmol) and *i*-Pr_2NEt (52 µL, 0.3 mmol)

in CH_2Cl_2 (3 mL). The reaction was allowed to warm slowly to rt over 19 h before being quenched with 0.1 M aq. HCl (10 mL). The layers were separated and the aqueous extracted with CH_2Cl_2 (×2). The combined organics were dried over $MgSO_4$, filtered and concentrated under reduced pressure (water bath < 30 °C). The crude product was purified by column chromatography (Petrol/Et_2O, 60:40) to give the title compound (108 mg, 87%, 90:10 dr) as a colourless oil. $[\alpha]_D^{22}$ 8.0 (*c* 1.0, $CHCl_3$); ν_{max} (neat) 1718 (C=O), 1355 (C-N), 1150 (R-SO_2N); HPLC analysis, Chiralpak IA (hexane/*i*-PrOH 95:5, 1.5 mLmin^{-1}, 211 nm, 40 °C) t_R (2*S*,5*S*): 24.2 min, t_R (2*R*,5*R*): 27.2 min, 98.5:1.5 er; ^{1}H NMR (400 MHz, CD_2Cl_2) δ_H: 1.16 (3H, t, *J* 7.1, OCH_2CH_3), 1.41 (3H, t, *J* 7.5, $SO_2CH_2CH_3$), 3.55 (1H, dq, *J* 14.4, 7.4, $SO_2CH^AH^B$), 3.78 (1H, dt, *J* 14.9, 7.5, $SO_2CH^AH^B$), 3.84–3.89 (1H, m, C(4)*H*), 4.12 (2H, q, *J* 7.1, OCH_2CH_3), 4.27 (1H, d, *J* 7.9, C(3)*H*), 5.83 (1H, dd, *J* 5.6, 1.5, C(5)*H*), 7.27–7.48 (10H, m, Ar*H*); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) δ_C: 7.3 ($SO_2CH_2CH_3$), 13.7 (OCH_2CH_3), 44.8 (*C*(4)H), 51.0 (SO_2CH_2), 53.2 (*C*(3)H), 61.7 (OCH_2), 115.3 (*C*(5)H), 125.5 (Ar*C*H), 128.0 (Ar*C*H), 128.3 (Ar*C*H), 128.5 (Ar*C*H), 128.6 (Ar*C*H), 128.8 (Ar*C*H), 135.3 (Ar*C*), 137.2 (*C*(6)), 140.8 (Ar*C*), 170.8 (*C*(2)), 172.9 (CO_2Et); *m/z* (NSI$^+$) 413 ([M+Na]$^+$, 100%); HMRS (NSI$^+$) $C_{22}H_{23}NO_5SNa$ [M+Na]$^+$ found 436.1185, requires 436.1189 (–1.0 ppm).

Crossover Experiment

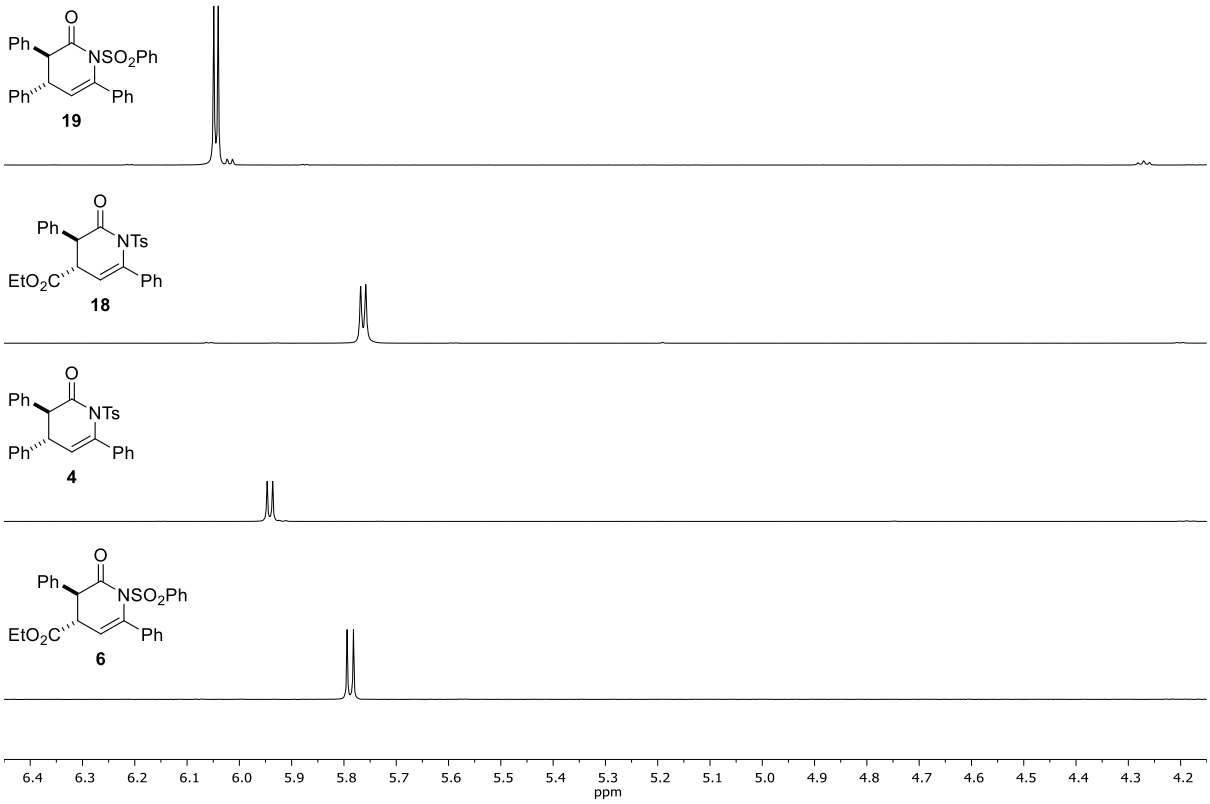


Fig. S3 ^{1}H NMR overlay of *N*-sulfonyl dihydropyridinones **4**, **6**, **18**, and **19**

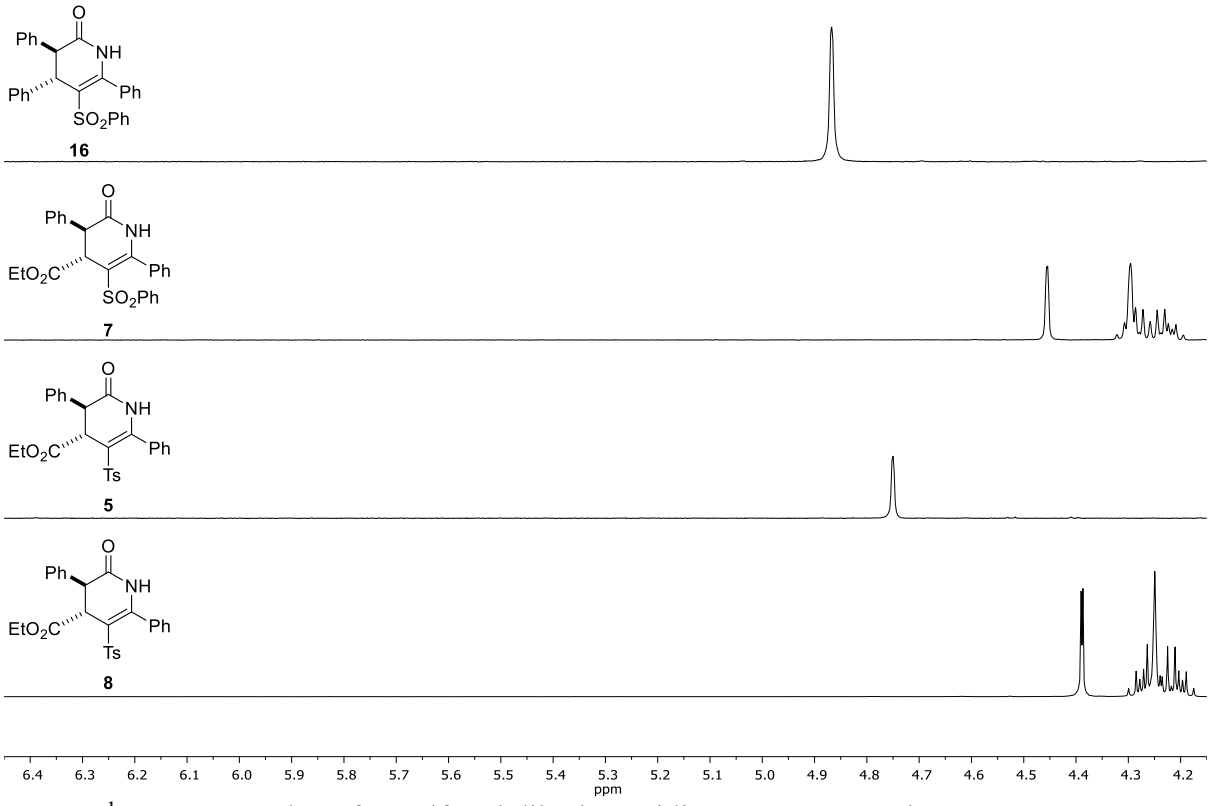


Fig. S4 ^{1}H NMR overlay of *C*-sulfonyl dihydropyridinones **5**, **7**, **8**, and **16**

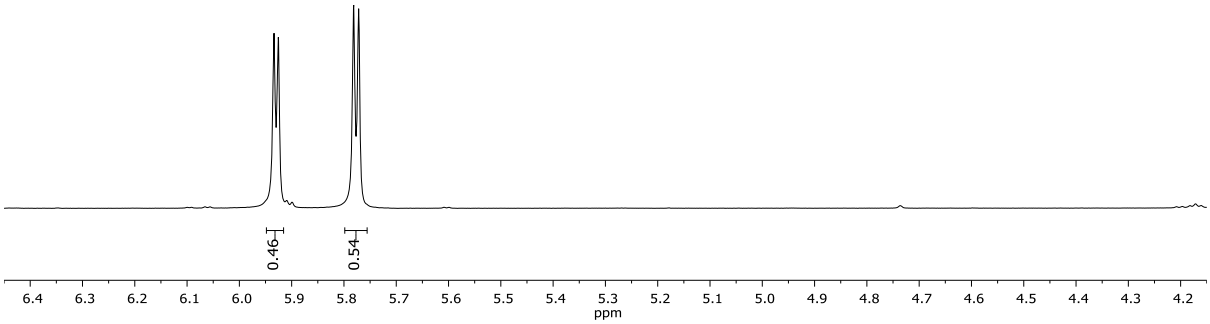


Fig. S5 ^{1}H NMR of crossover experment, t = 0

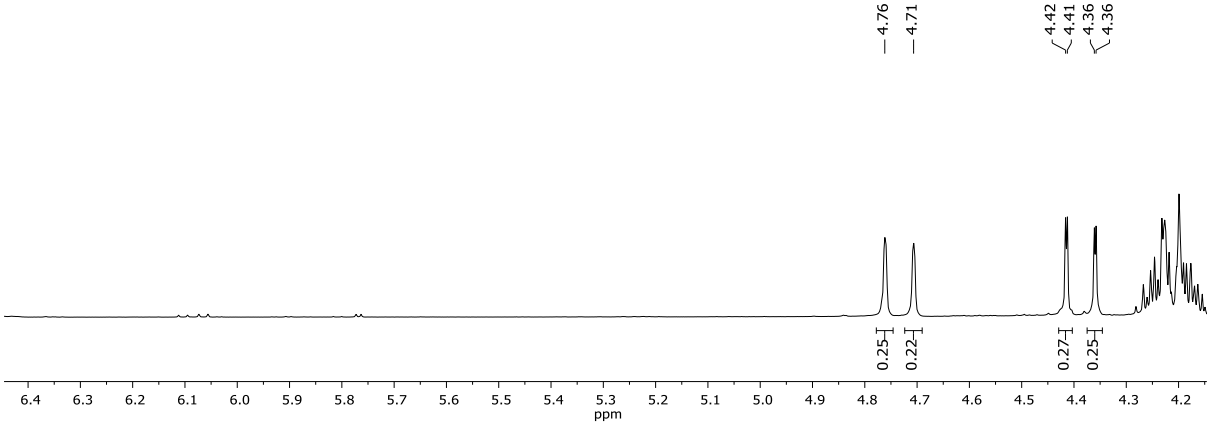


Fig. S6 ^{1}H NMR of crossover experiment, t = 18 h

UV/Vis Spectroscopy

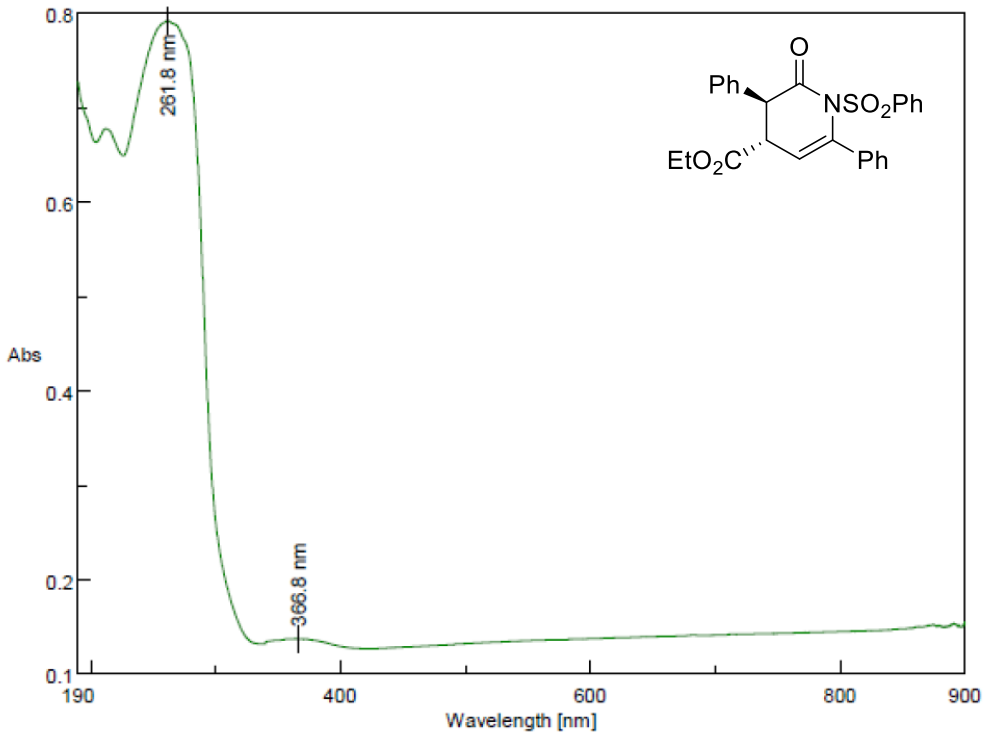


Fig. S7 UV/Vis spectrum of dihydropyridinone **6**

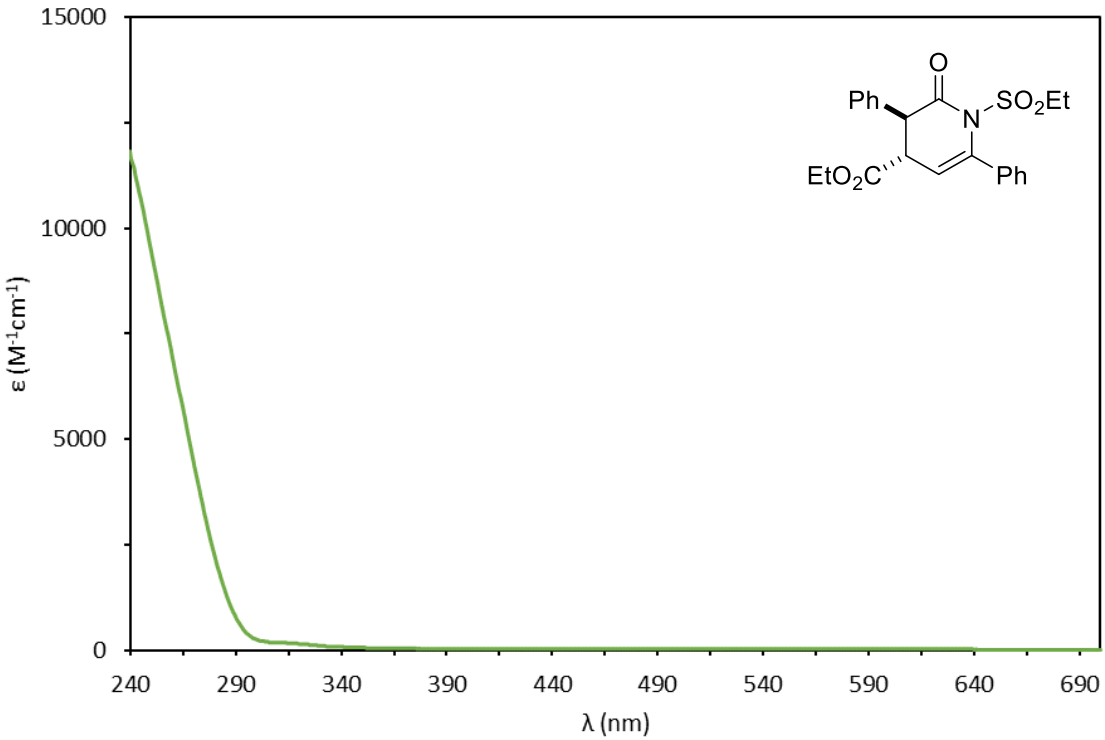
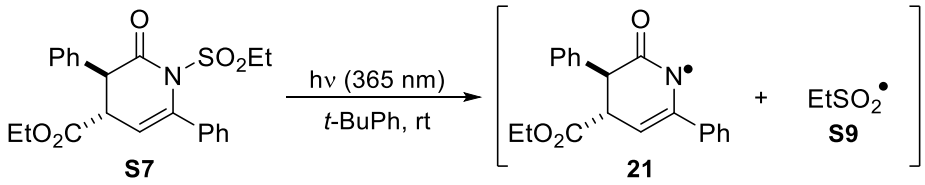


Fig. S8 UV/Vis spectrum of dihydropyridinone **S7**

EPR Analysis of Dihydropyridinone S7

Dihydropyridinone **S7** (10 mg) was was disolved in PhBu-*t* (0.5 mL). A 0.2 mL sample was transferred to a quartz tube (0.4 mm dia.) and de-aerated by bubbling nitrogen for ca. 15 min. This tube was placed in the resonant cavity of the EPR spectrometer and irradiated with the full spectrum from a 500 Watt high pressure Hg arc. Isotropic EPR spectra were scanned repeatedly at several temperatures (295 K, 265 K and 250 K). The EPR settings were: Microwave Frequency = 9.46 GHz Microwave Power = 4.0 mW, Gain = $2e^6$, Modulation Amplitude =0.8 Gpp, Time constant = 10 ms, Scan time = 20 s. The spectra were computer simulated with the NIEHS software package WinSim2002. A large central broad feature, probably due to radicals trapped and immobilised in the solid particles in the dispersion, was removed by digital filtration.



Scheme S1 EPR study of the photoisomerisation of dihydropyridinone **S7**

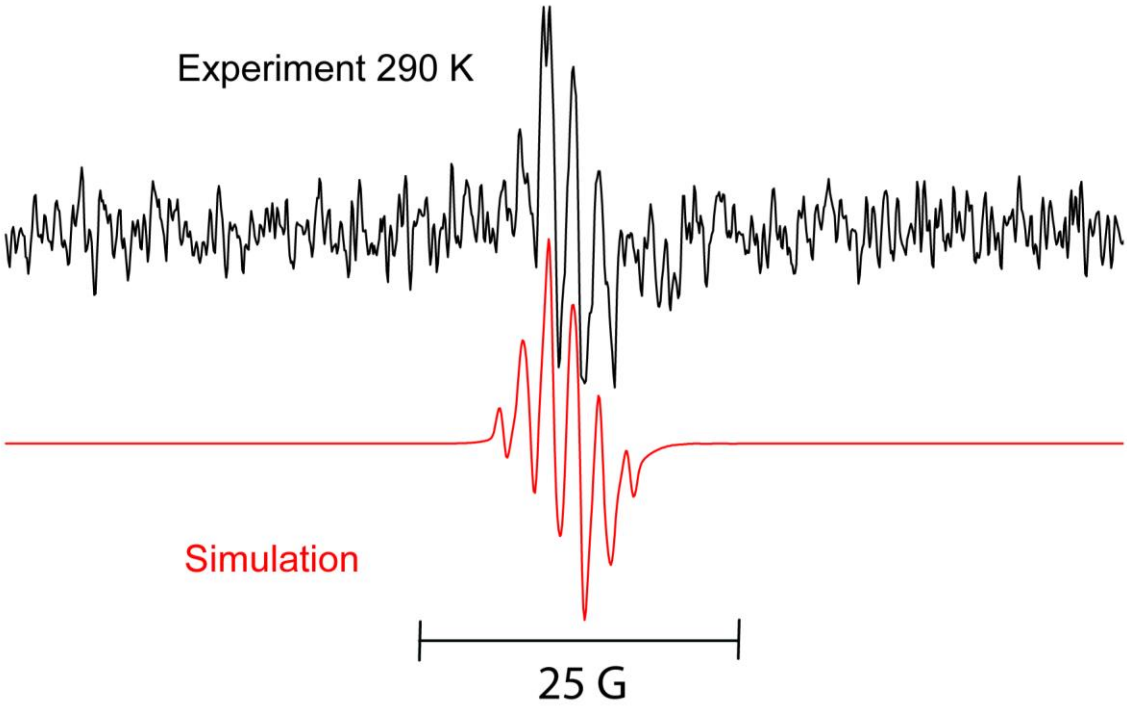


Fig. S9 EPR spectra during continuous photolysis of a solution of dihydropyridinone **S7** in PhBu-*t* at 290 K after 100 scans. Top: Experimental 100 scans at 290 K. Bottom (red) Computer simulation.

References and Notes

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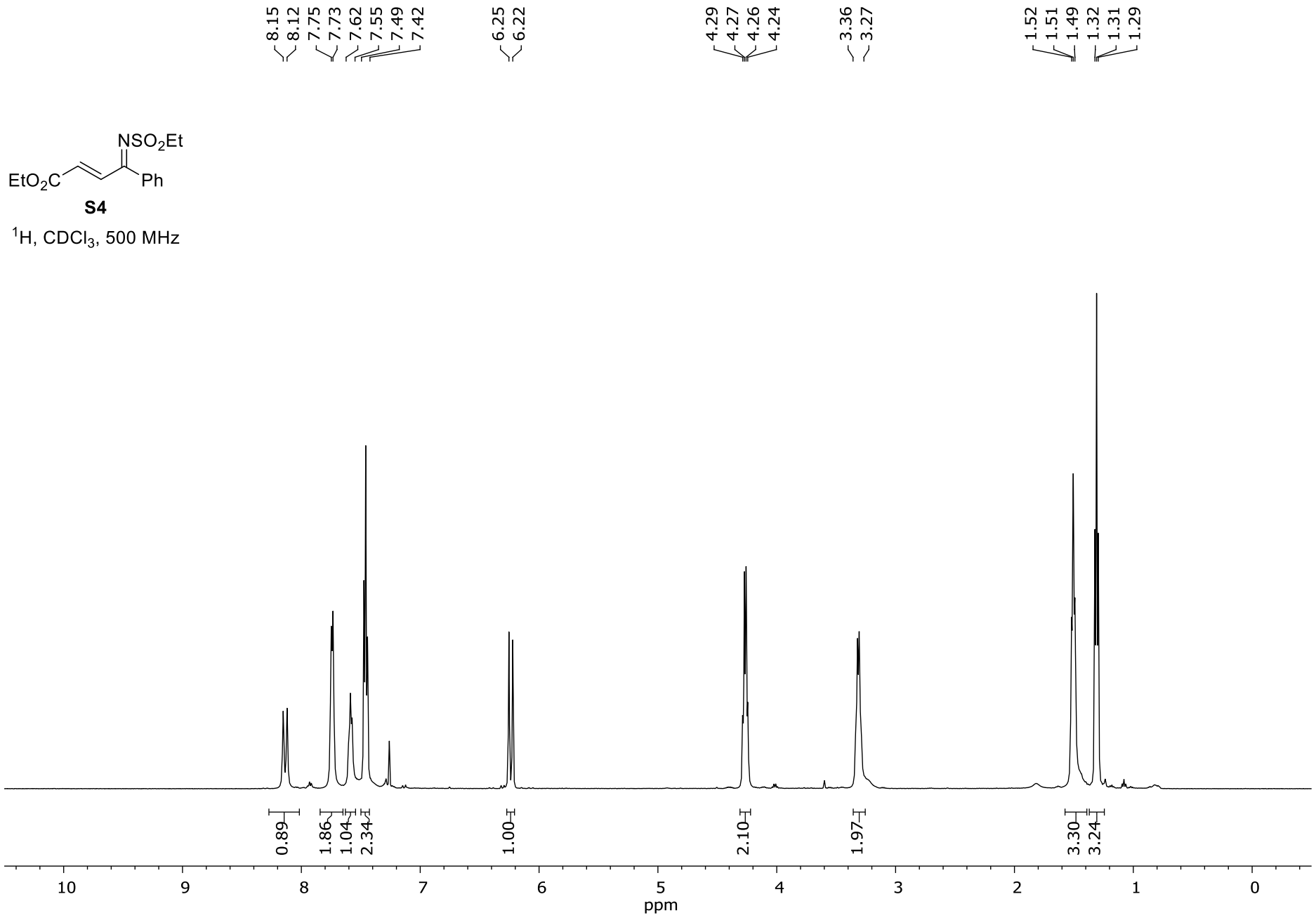
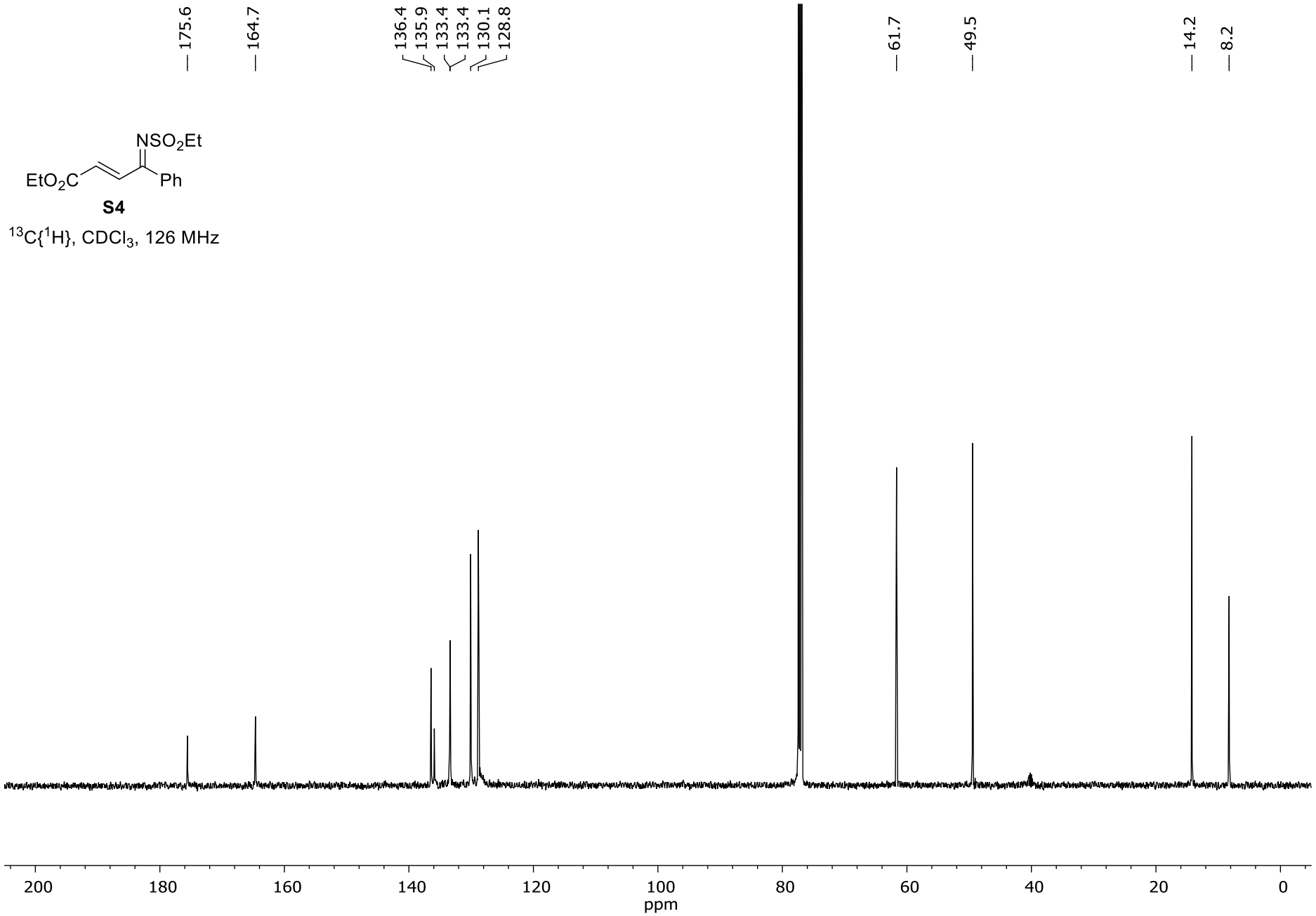
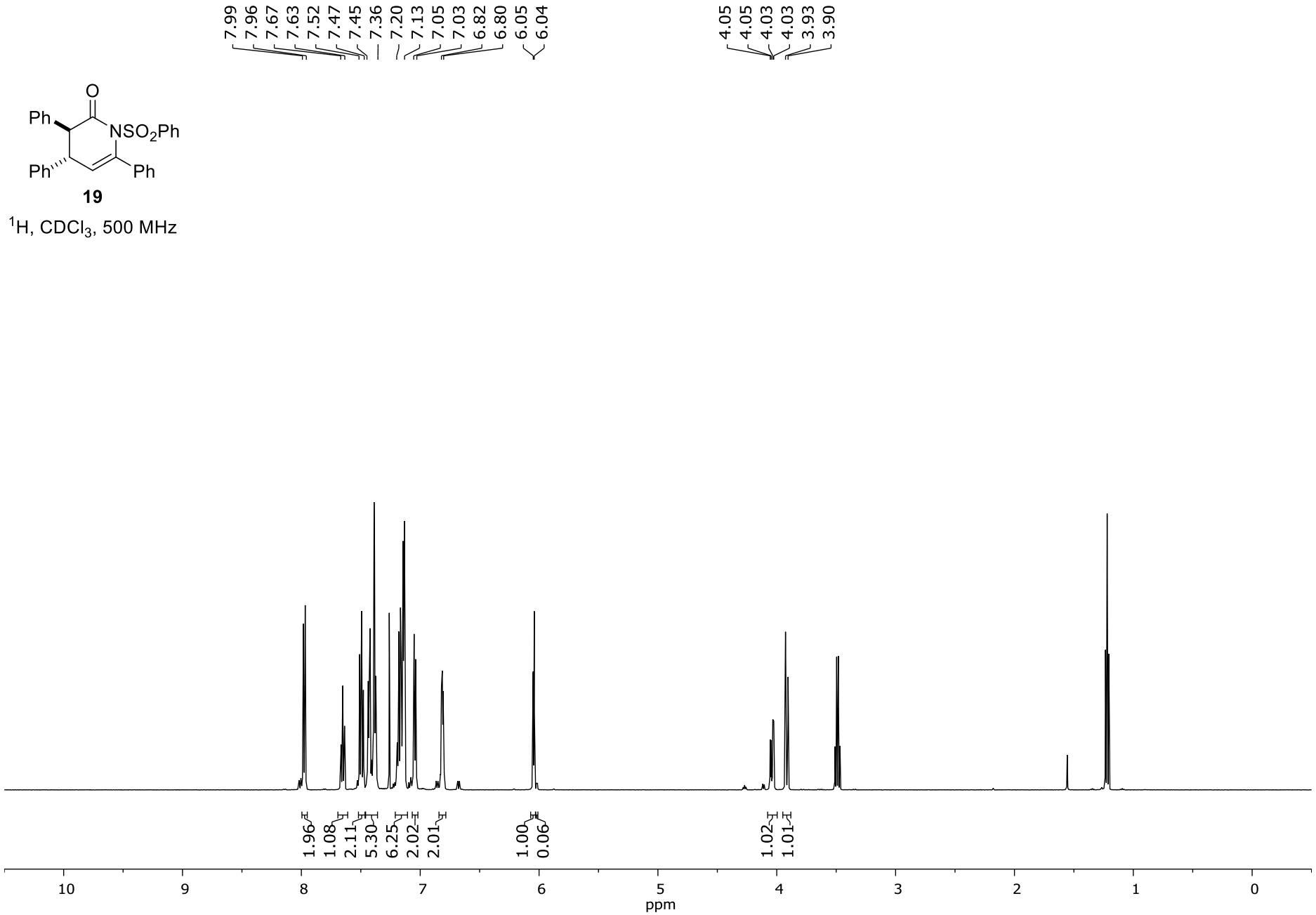
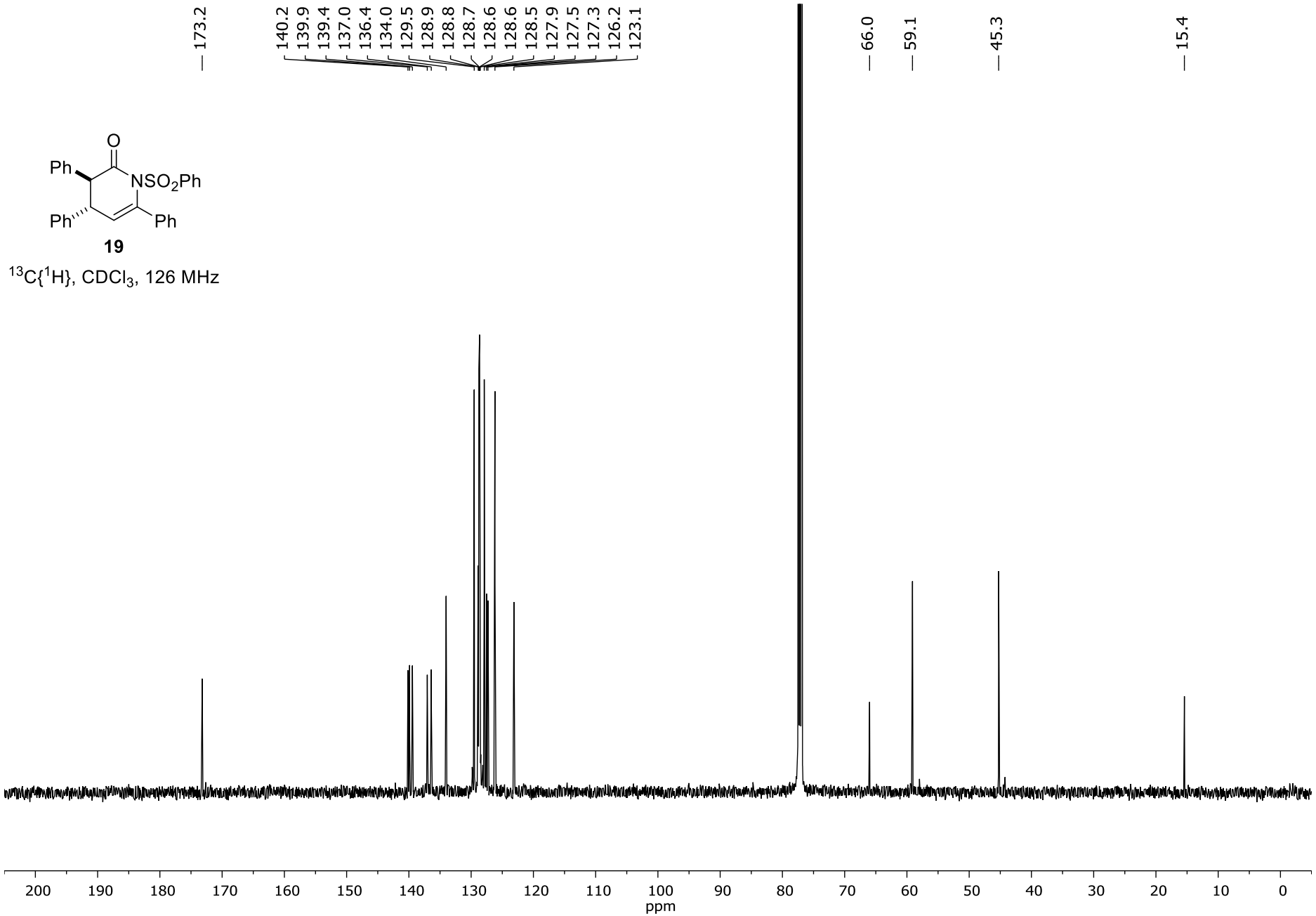
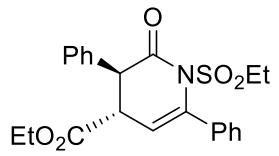

8.15
8.12
7.75
7.73
7.62
7.55
7.49
7.42
6.25
6.22
4.29
4.27
4.26
4.24
3.36
3.27
1.52
1.51
1.49
1.32
1.31
1.29
NSO2Et
EtO2C
Ph
S4
1H, CDCl3, 500 MHz
0.89
1.86
1.04
2.34
1.00
2.10
1.97
3.30
3.24
10
9
8
7
6
5
4
3
2
1
0
ppm


175.6
164.7
136.4
135.9
133.4
133.4
130.1
128.8
61.7
49.5
14.2
8.2
NSO2Et
EtO2C
Ph
S4
13C{1H}, CDCl3, 126 MHz
200
180
160
140
120
100
80
60
40
20
0
ppm

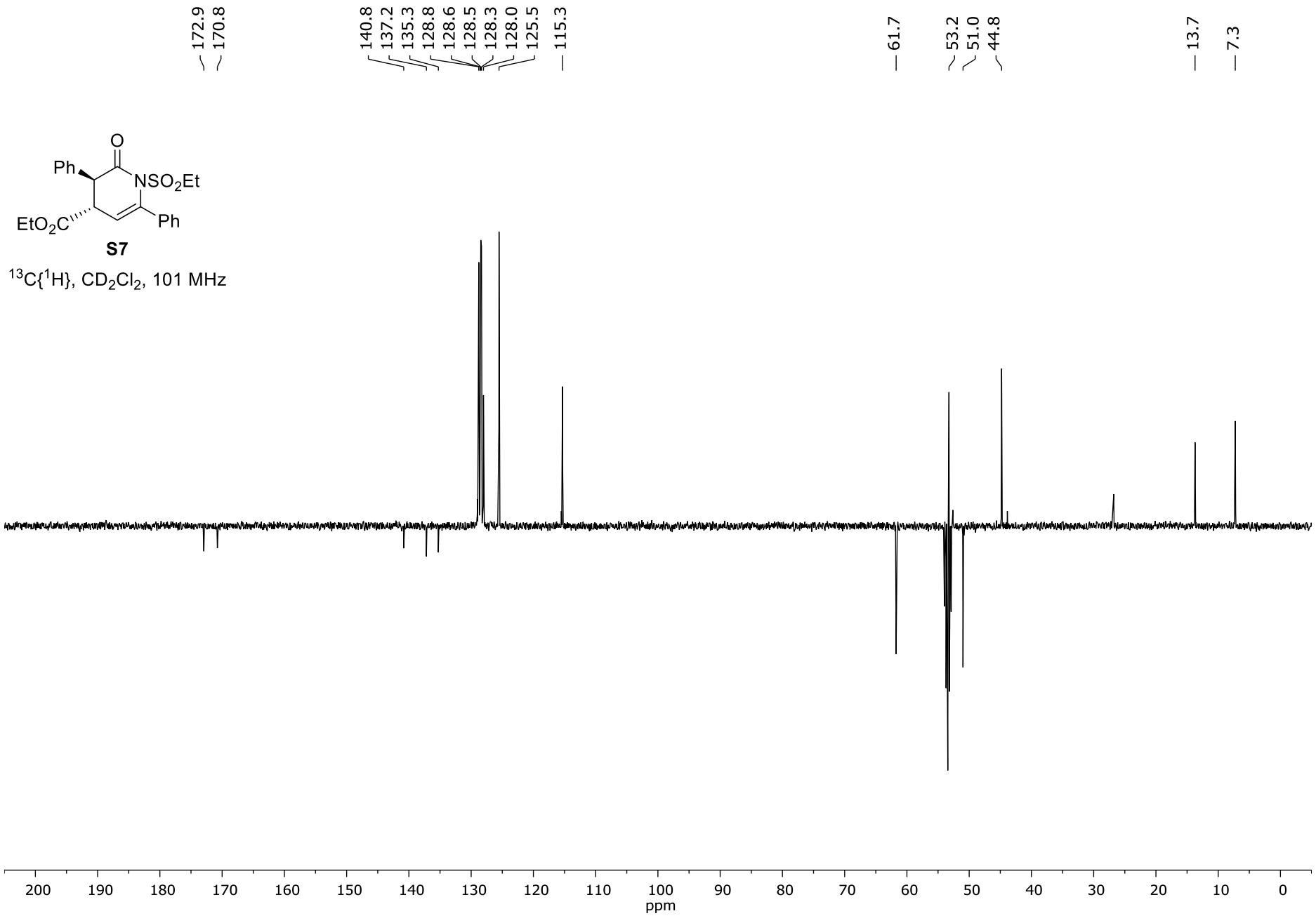

7.99
7.96
7.67
7.63
7.52
7.47
7.45
7.36
7.20
7.13
7.05
7.03
6.82
6.80
6.05
6.04
4.05
4.05
4.03
4.03
3.93
3.90
O
Ph
NSO2Ph
Ph
Ph
19
1H, CDCl3, 500 MHz
1.96
1.08
2.11
5.30
6.25
2.02
2.01
1.00
0.06
1.02
1.01
10
9
8
7
6
5
4
3
2
1
0
ppm


173.2
140.2
139.9
139.4
137.0
136.4
134.0
129.5
128.9
128.8
128.7
128.6
128.6
128.5
127.9
127.5
127.3
126.2
123.1
66.0
59.1
45.3
15.4
O
Ph
NSO2Ph
Ph
Ph
19
13C{1H}, CDCl3, 126 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



S7

^{1}H, CD_2Cl_2, 400 MHz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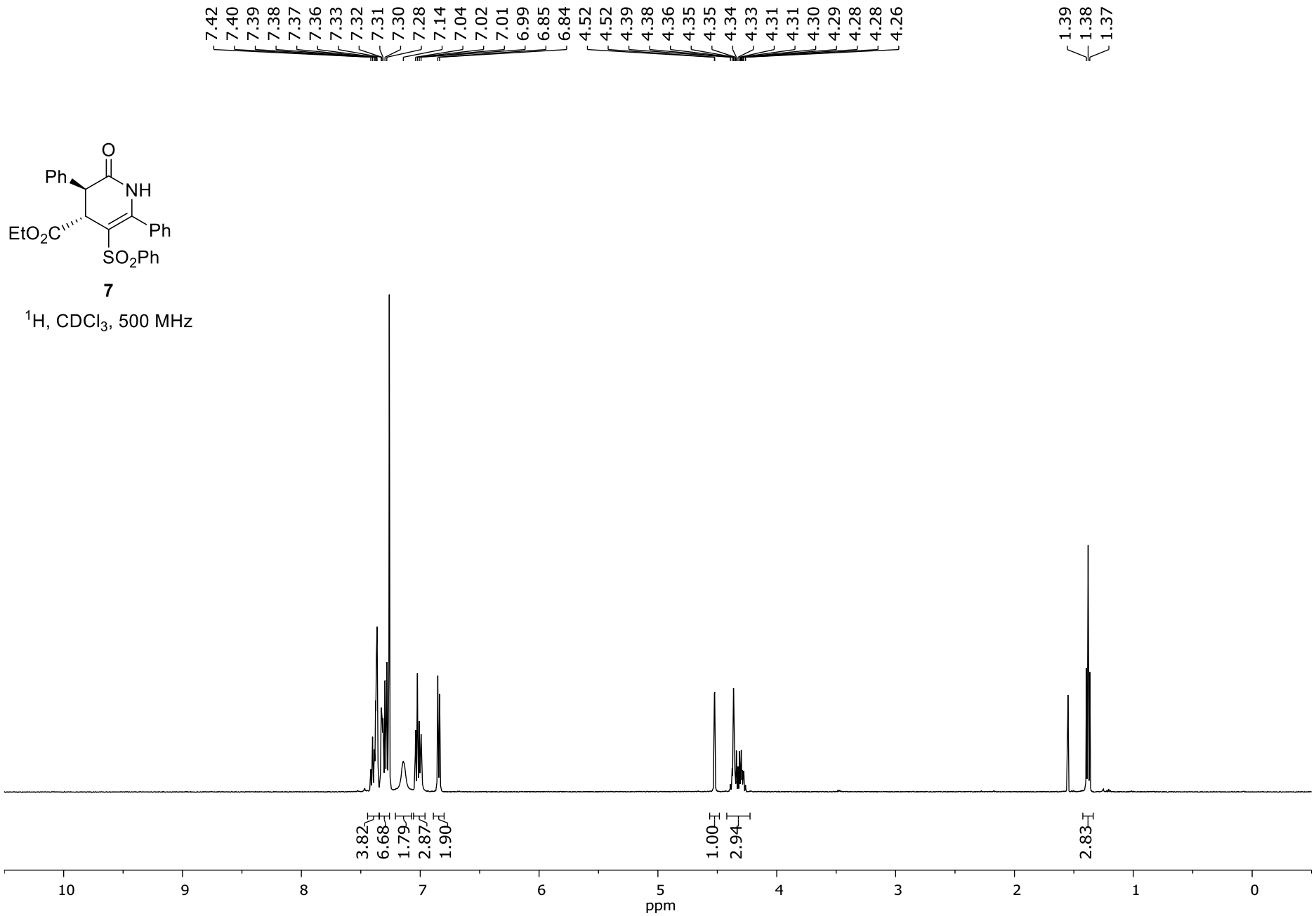
170.8
140.8
137.2
135.3
128.8
128.6
128.5
128.3
128.0
125.5
115.3
61.7
53.2
51.0
44.8
13.7
7.3
O
Ph
NSO2Et
EtO2C
Ph
S7
13C{1H}, CD2Cl2, 101 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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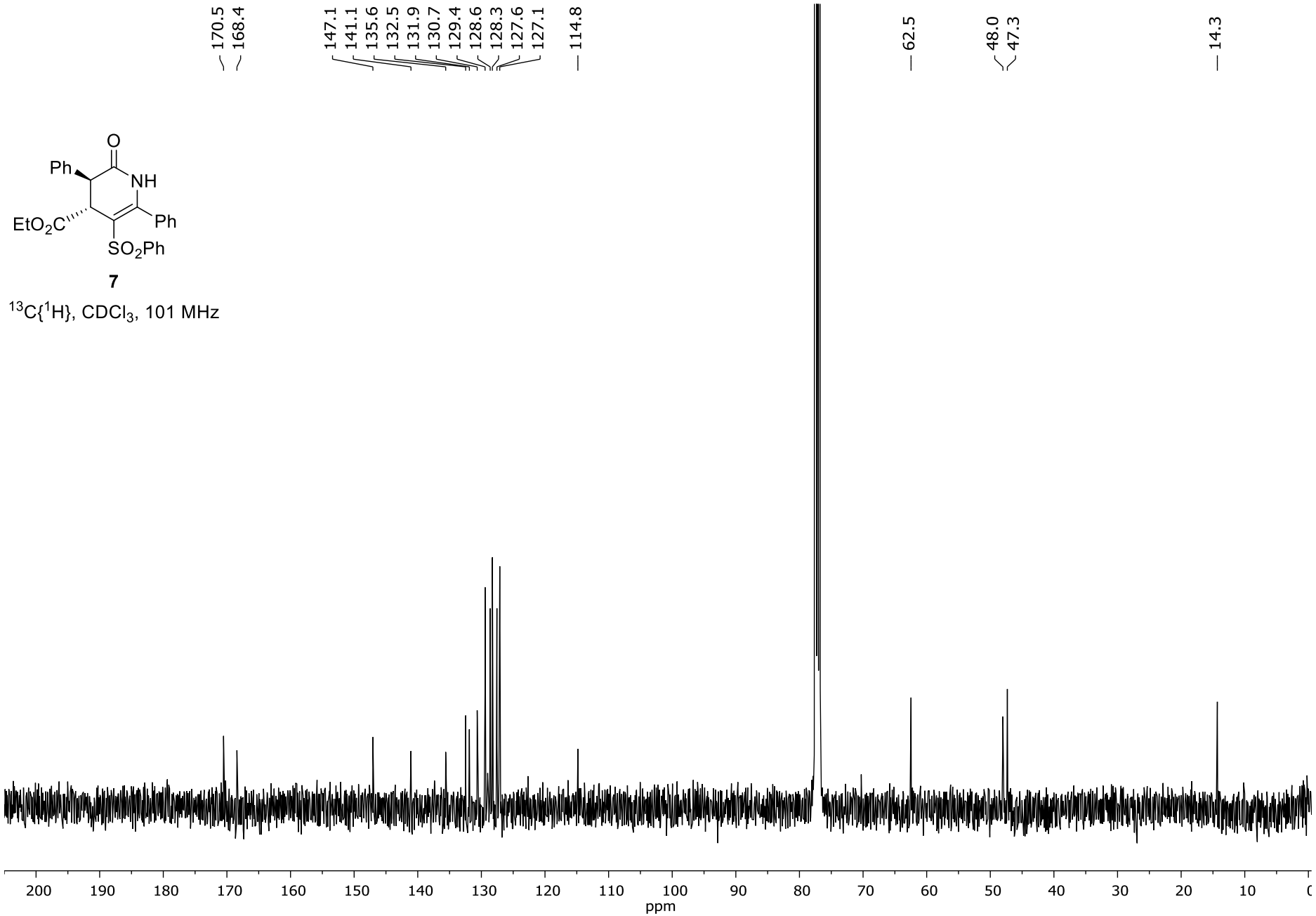
7.40
7.39
7.38
7.37
7.36
7.33
7.32
7.31
7.30
7.28
7.14
7.04
7.02
7.01
6.99
6.85
6.84
4.52
4.52
4.39
4.38
4.36
4.35
4.35
4.34
4.33
4.31
4.31
4.30
4.29
4.28
4.28
4.26
1.39
1.38
1.37
O
Ph
NH
EtO2C
Ph
SO2Ph
7
1H, CDCl3, 500 MHz
3.82
6.68
1.79
2.87
1.90
1.00
2.94
2.83
10
9
8
7
6
5
4
3
2
1
0
ppm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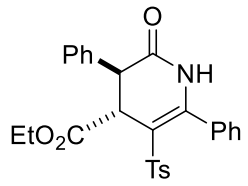
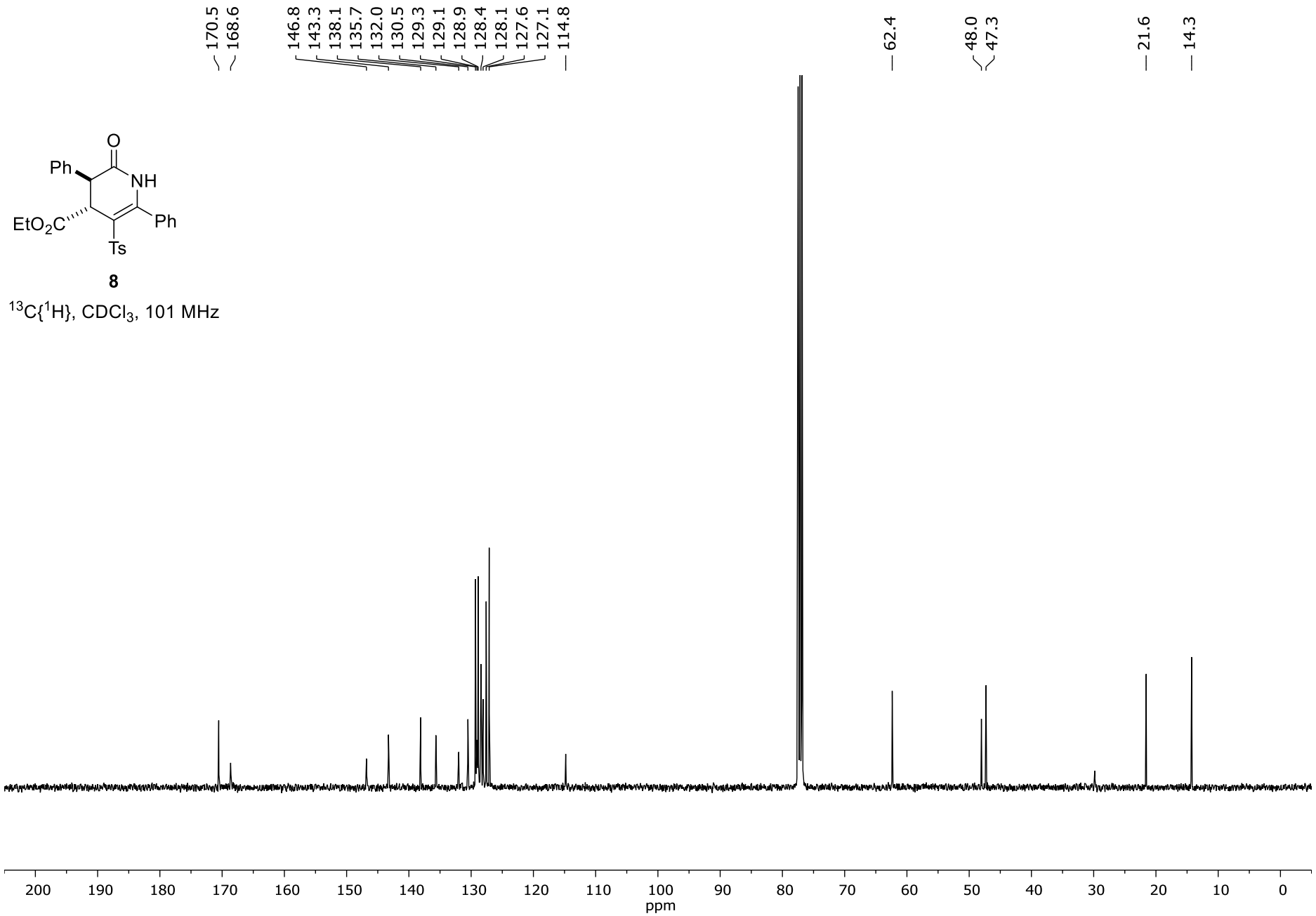
168.4
147.1
141.1
135.6
132.5
131.9
130.7
129.4
128.6
128.3
127.6
127.1
114.8
62.5
48.0
47.3
14.3
O
Ph
NH
EtO2C
Ph
SO2Ph
7
13C{1H}, CDCl3, 101 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



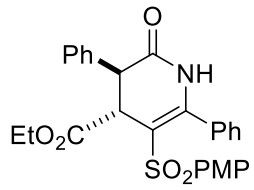
8

^{1}H, $CDCl_3$, 400 MHz



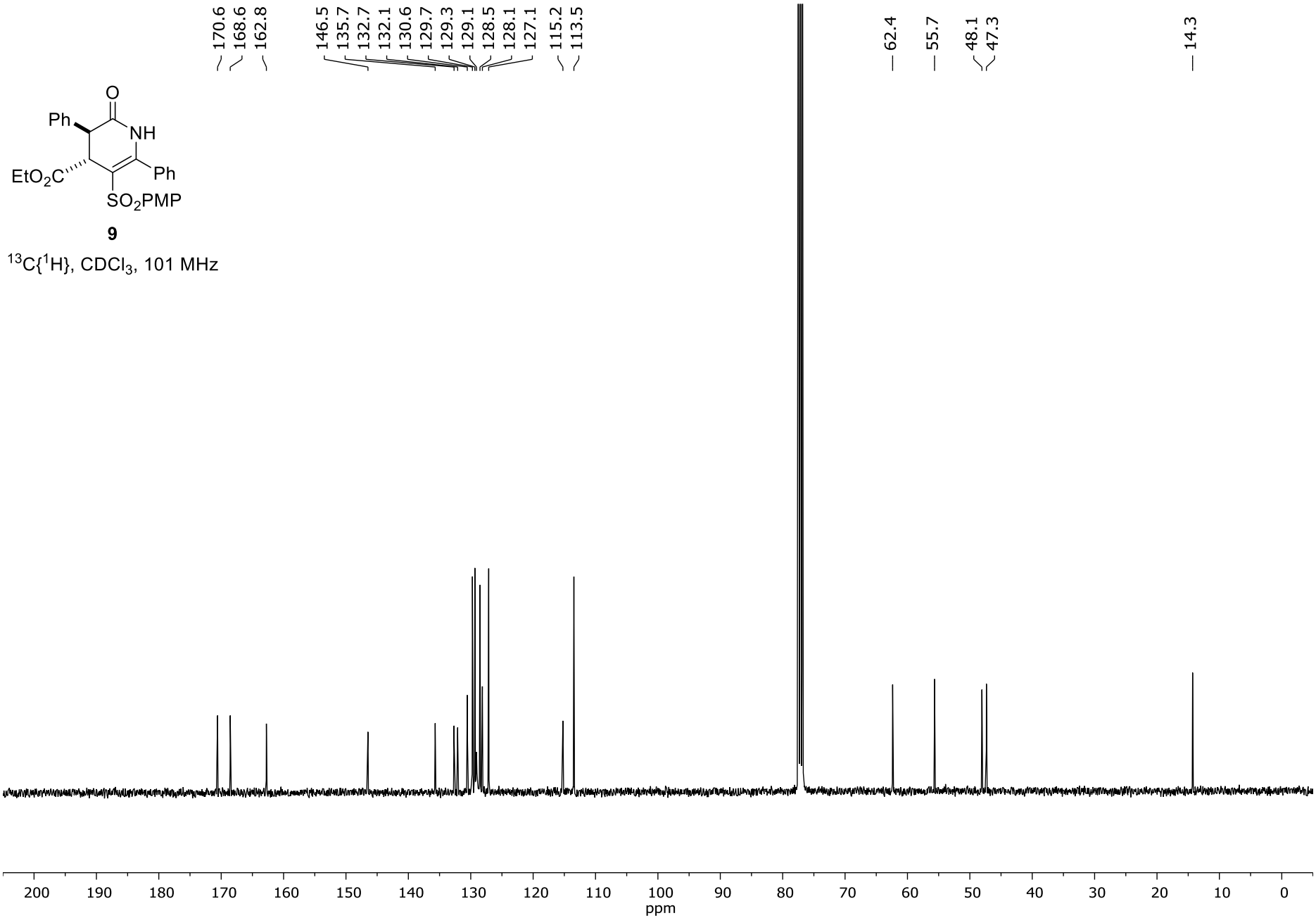
8

$^{13}C\{^{1}H\}$, $CDCl_3$, 101 MHz



9

^{1}H, $CDCl_3$, 400 MHz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168.6
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146.5
135.7
132.7
132.1
130.6
129.7
129.3
129.1
128.5
128.1
127.1
115.2
113.5
62.4
55.7
48.1
47.3
14.3
O
Ph
NH
Ph
EtO2C
SO2PMP
9
13C{1H}, CDCl3, 101 MHz
200
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150
140
130
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110
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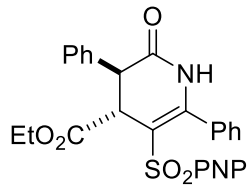
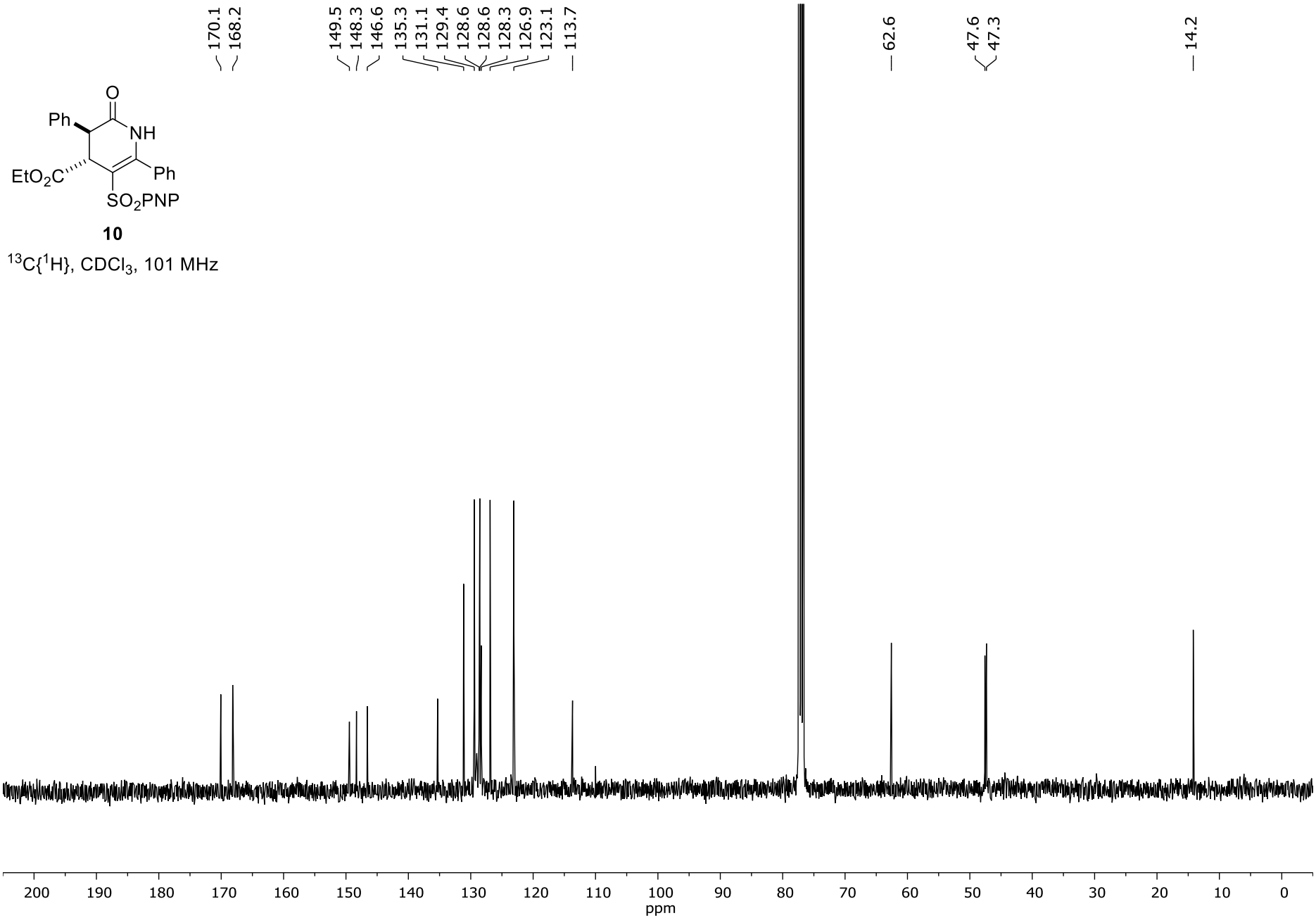
30
20
10
0
ppm



10

^{1}H, $CDCl_3$, 400 MHz


170.1
168.2
149.5
148.3
146.6
135.3
131.1
129.4
128.6
128.6
128.3
126.9
123.1
113.7
62.6
47.6
47.3
14.2
O
Ph
NH
Ph
EtO2C
SO2PNP
10
13C{1H}, CDCl3, 101 MHz
200
190
180
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150
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100
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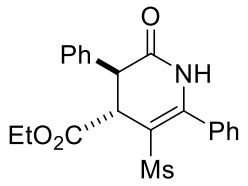
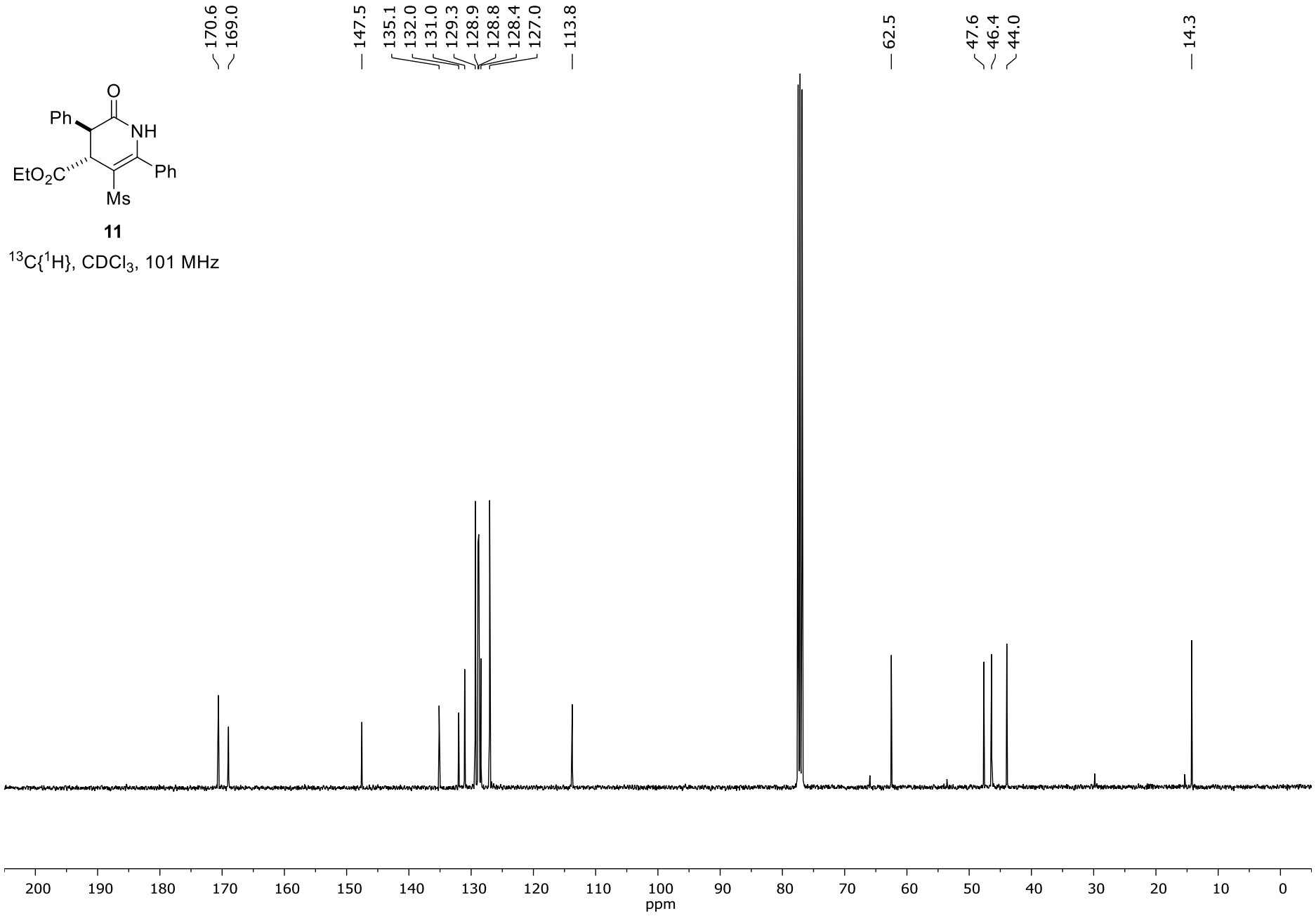
30
20
10
0
ppm



11

^{1}H, $CDCl_3$, 500 MHz


170.6
169.0
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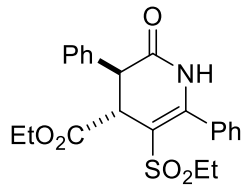
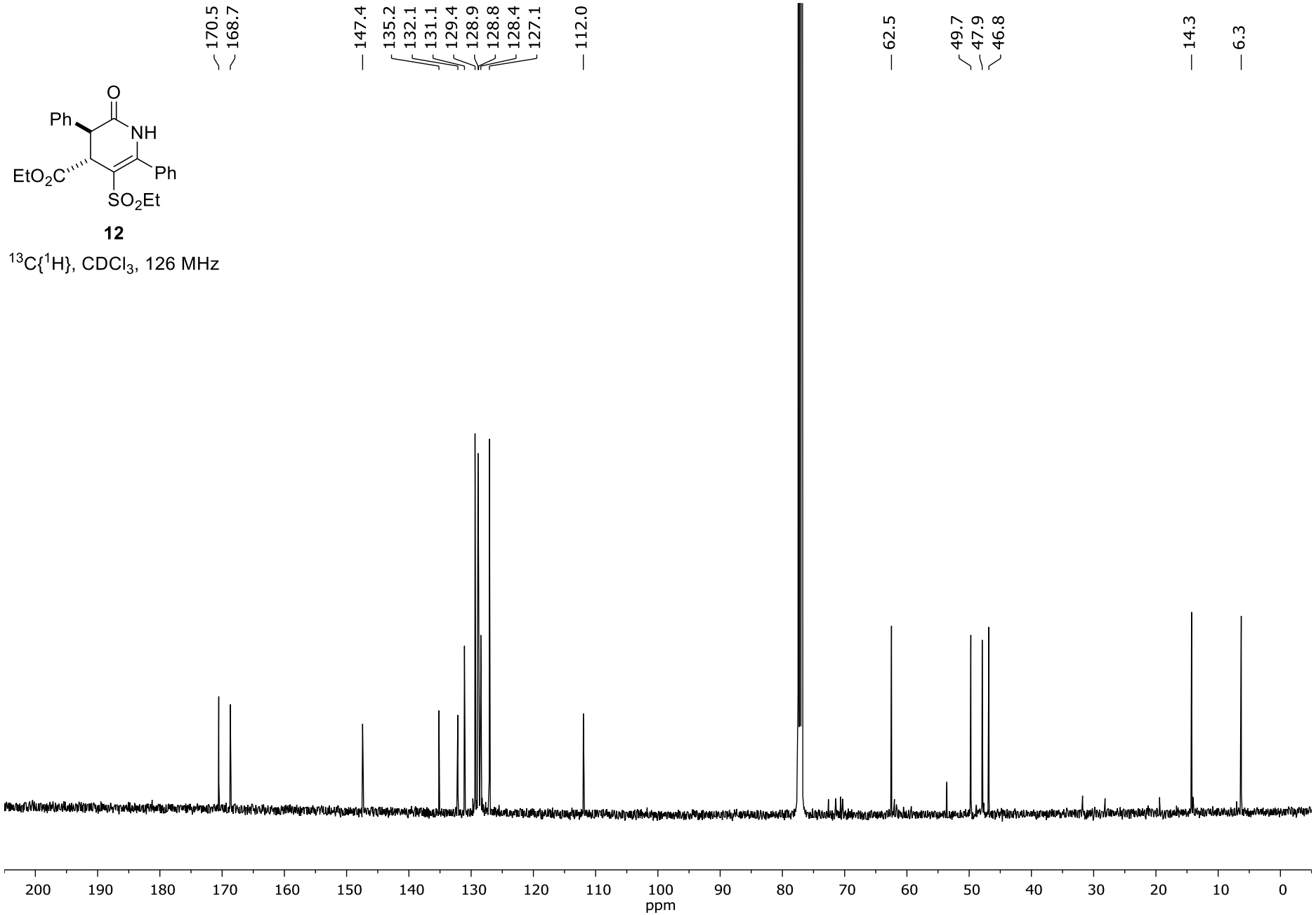
135.1
132.0
131.0
129.3
128.9
128.8
128.4
127.0
113.8
62.5
47.6
46.4
44.0
14.3
O
Ph
NH
Ph
EtO2C
Ms
11
13C{1H}, CDCl3, 101 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



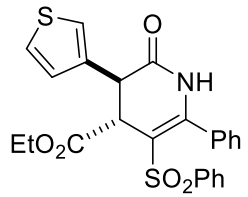
12

^{1}H, $CDCl_3$, 500 MHz



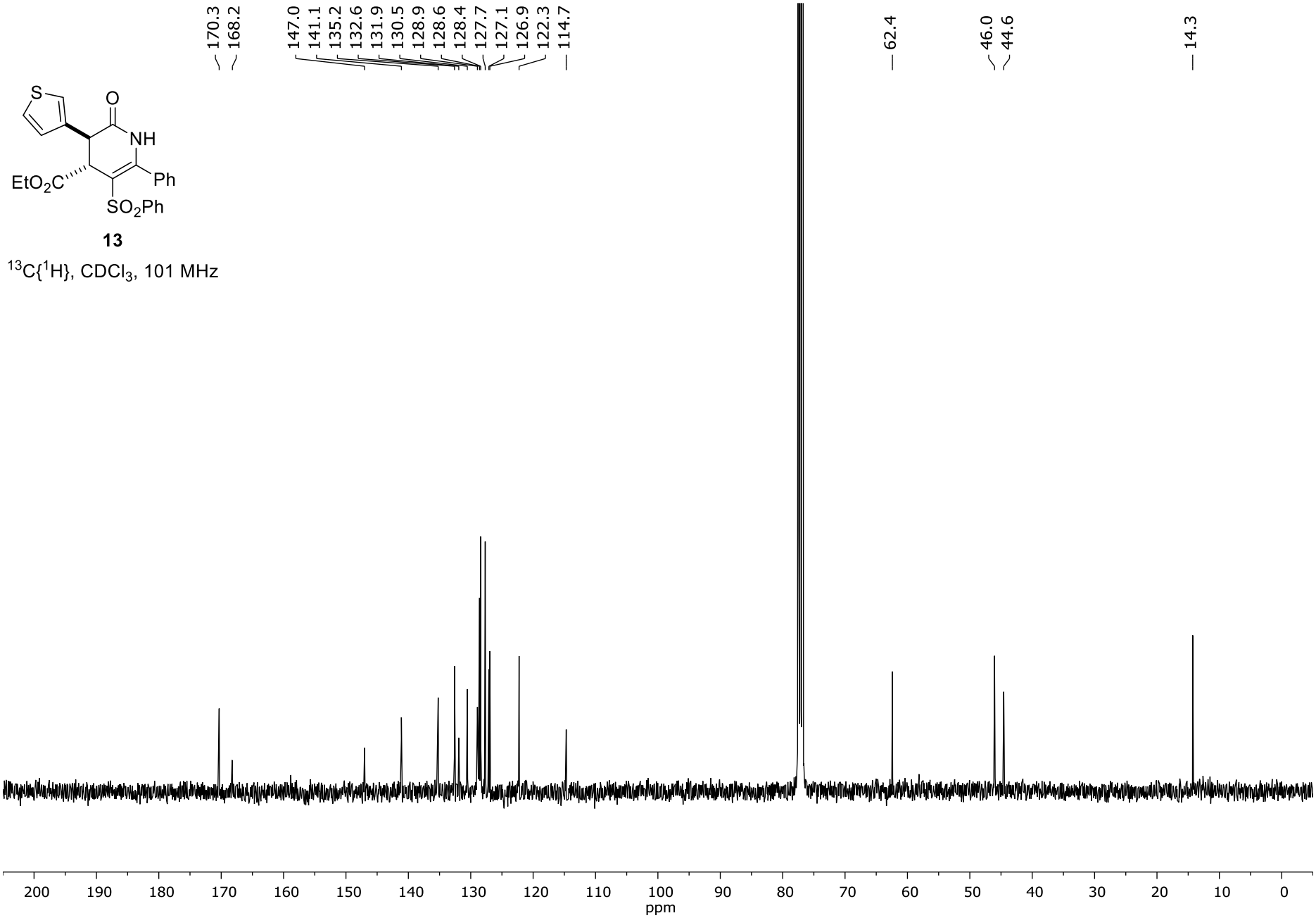
12

$^{13}C\{^{1}H\}$, $CDCl_3$, 126 MHz



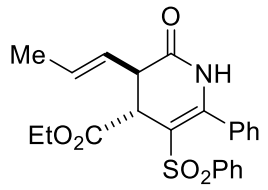
13

^{1}H, $CDCl_3$, 400 MHz



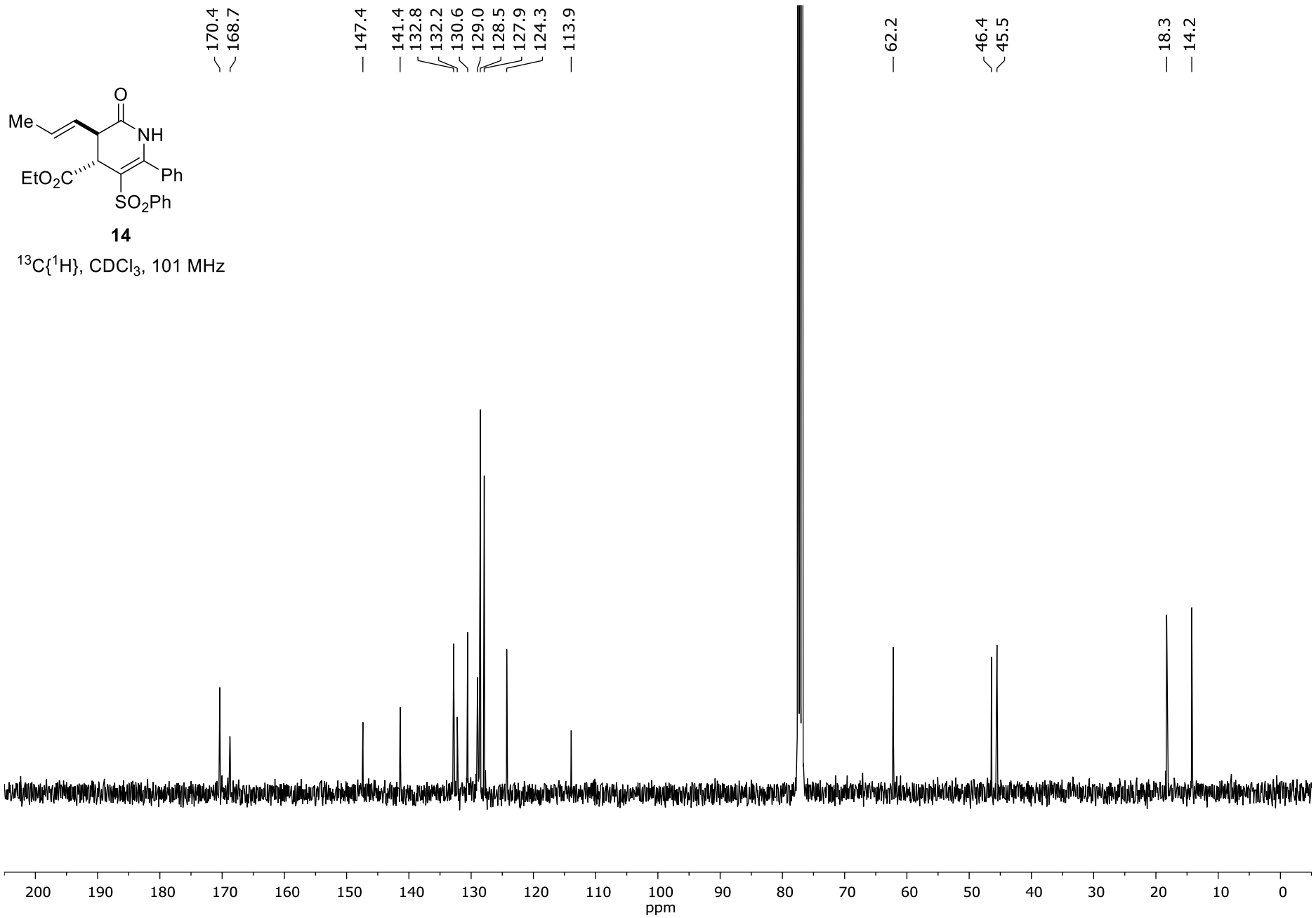
13

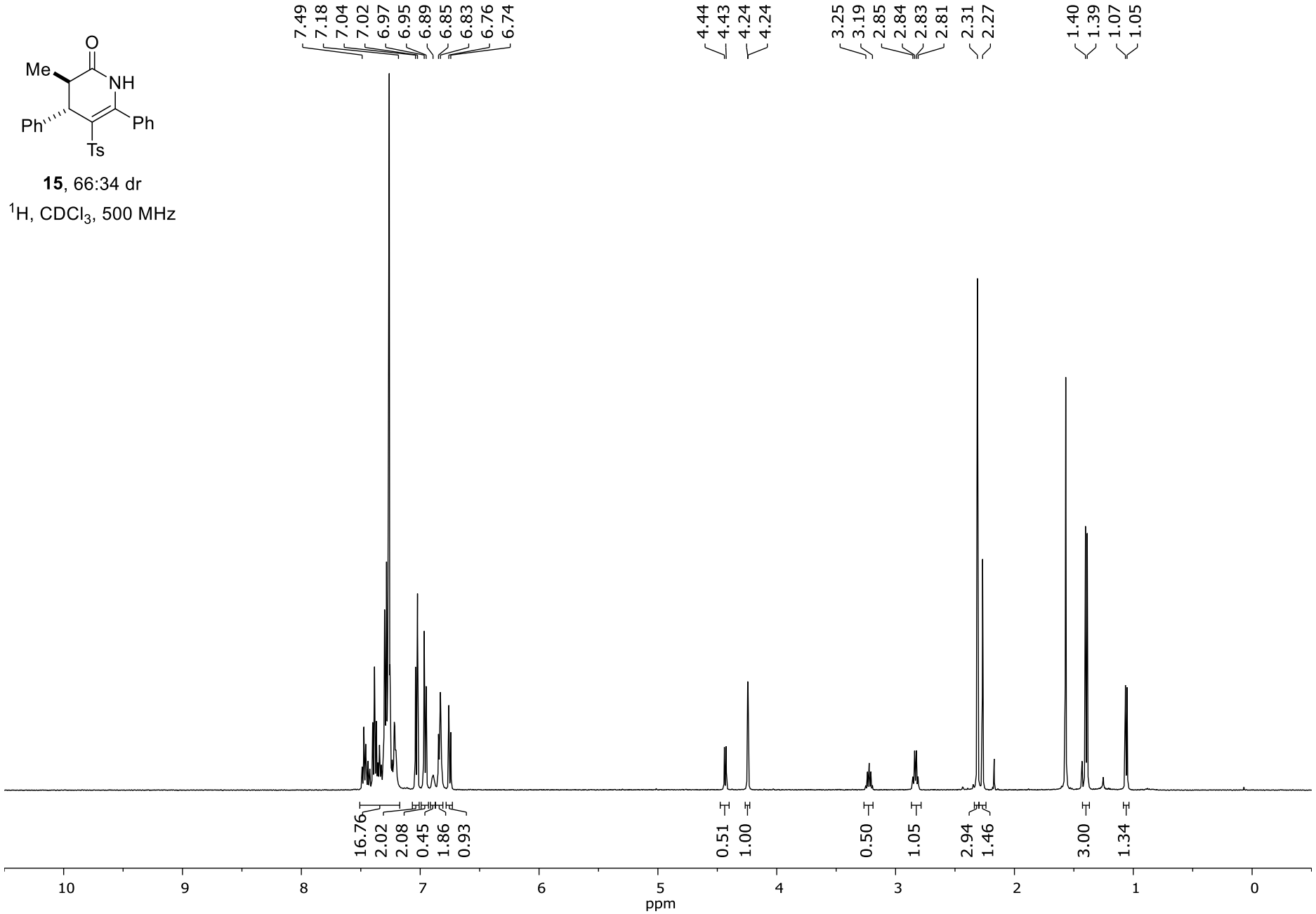
$^{13}C\{^{1}H\}$, $CDCl_3$, 101 MHz

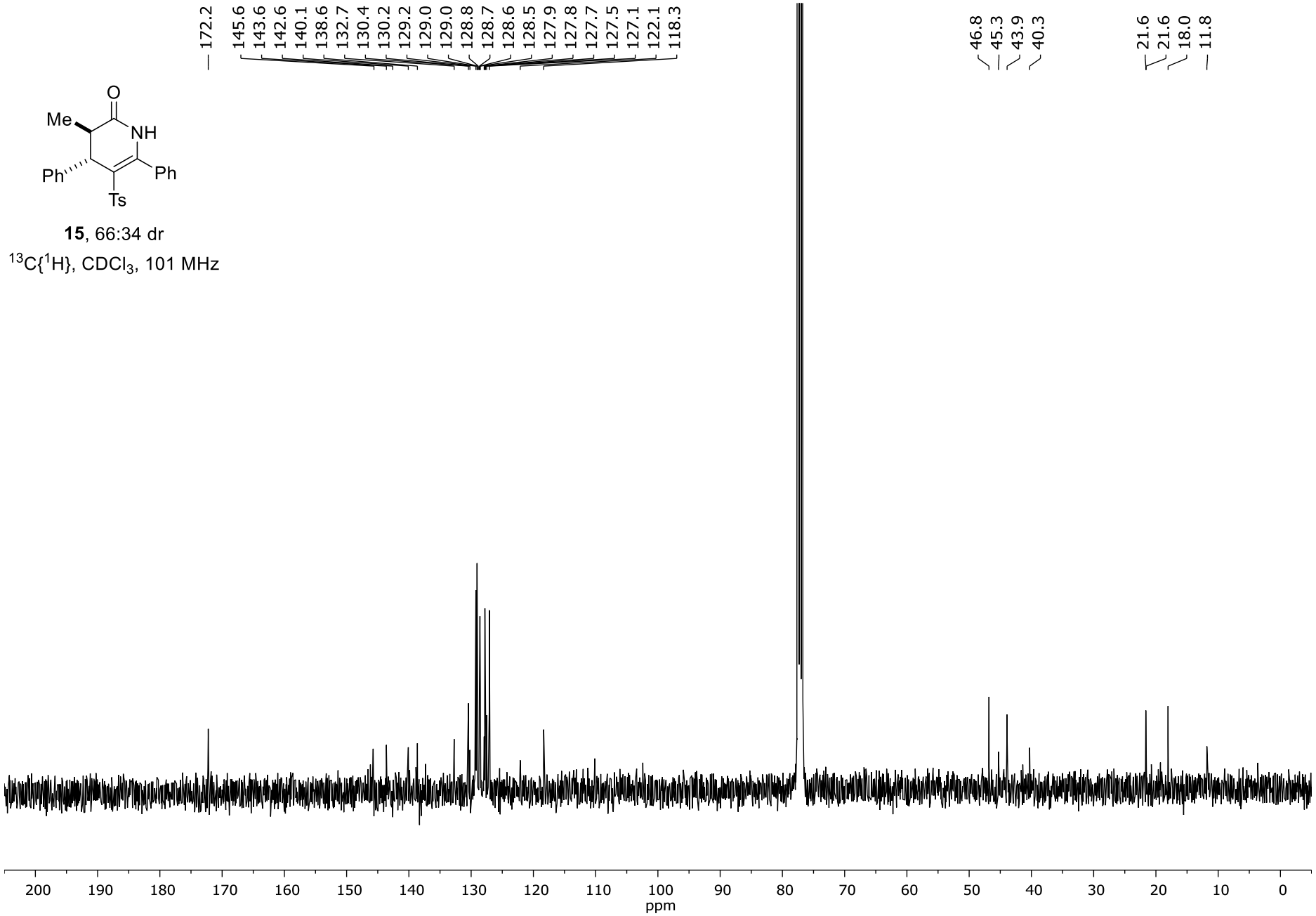


14

^{1}H, $CDCl_3$, 400 MHz

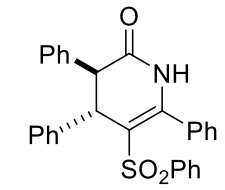

170.4
168.7
147.4
141.4
132.8
132.2
130.6
129.0
128.5
127.9
124.3
113.9
62.2
46.4
45.5
18.3
14.2
Me
O
NH
Ph
EtO2C
SO2Ph
14
13C{1H}, CDCl3, 101 MHz
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


O
Me
NH
Ph
Ph
Ts
15, 66:34 dr
1H, CDCl3, 500 MHz
7.49
7.18
7.04
7.02
6.97
6.95
6.89
6.85
6.83
6.76
6.74
4.44
4.43
4.24
4.24
3.25
3.19
2.85
2.84
2.83
2.81
2.31
2.27
1.40
1.39
1.07
1.05
16.76
2.02
2.08
0.45
1.86
0.93
0.51
1.00
0.50
1.05
2.94
1.46
3.00
1.34
10
9
8
7
6
5
4
3
2
1
0
ppm



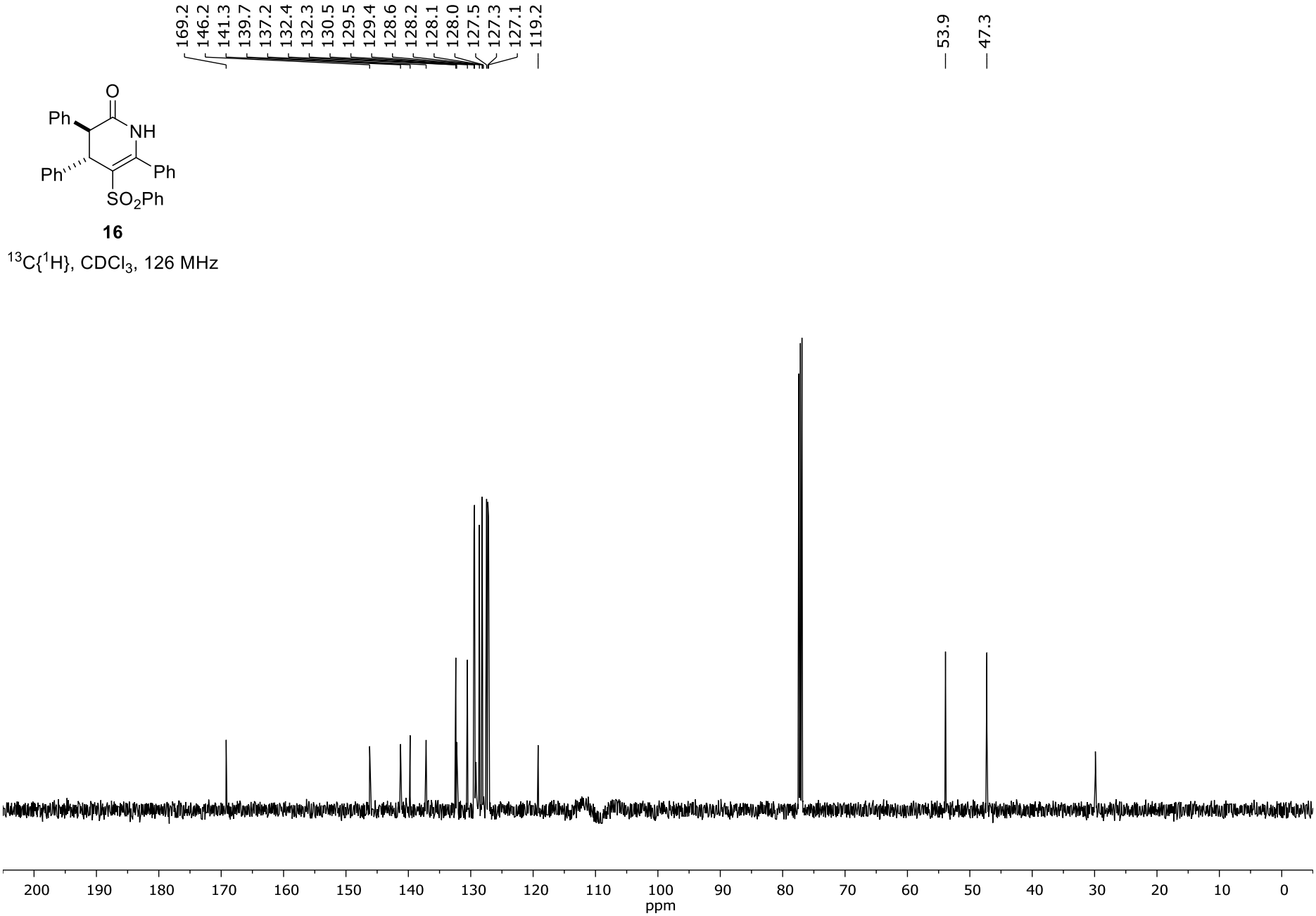
15, 66:34 dr

$^{13}C\{^{1}H\}$, $CDCl_3$, 101 MHz



16

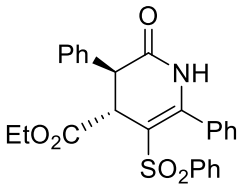
^{1}H, $CDCl_3$, 500 MHz



16

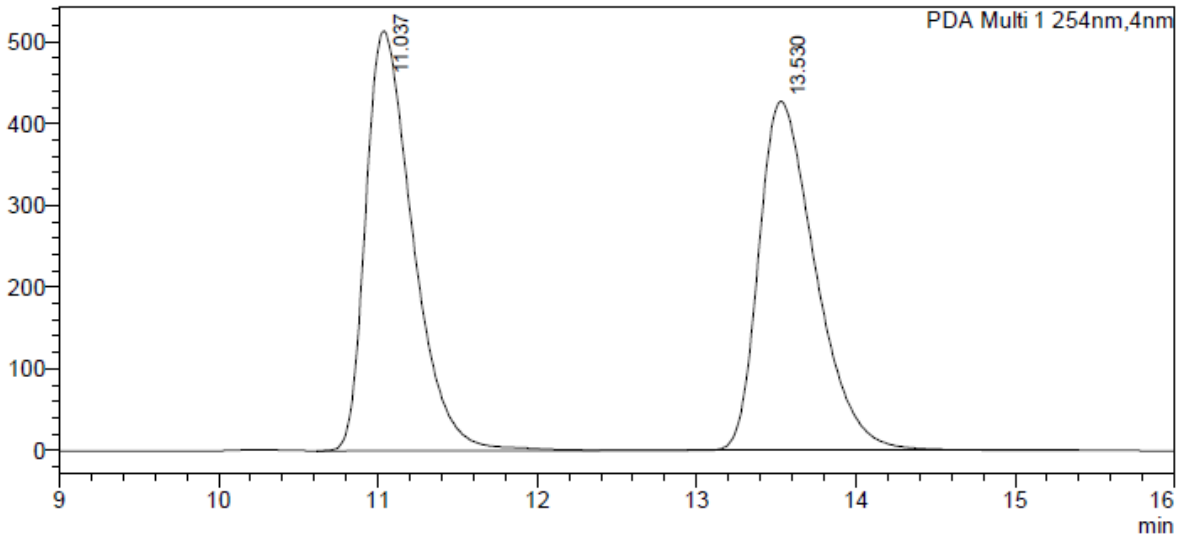
$^{13}C\{^{1}H\}$, $CDCl_3$, 126 MHz

HPLC data for **7**. Chiralpak IA (70:30 hexane/*i*-PrOH, 1.0 mLmin^{-1}, 254 nm, 30 °C) t_R (3*R*,4*R*) 11.4 min, t_R (3*S*, 4*S*) 13.7 min, 99:1 er



PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	11.037	49.994
2	13.530	50.006
Total		100.000



PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	11.356	1.169
2	13.666	98.831
Total		100.000