NICKEL CATALYZED CYCLOADDITIVE COUPLING OF ENYNES AND ISOCYANATES

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Supporting Information

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General Experimental 1:

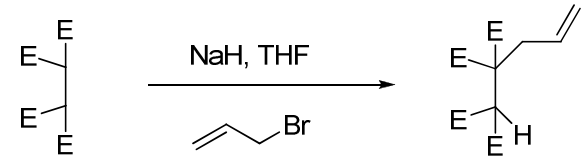
All reactions were carried out in the dry glove box until otherwise specified. Toluene was dried over neutral alumina under N_2 using a Grubbs type solvent purification system. THF was freshly distilled from Na/benzophenone. $Ni(COD)_2$ was purchased from Strem and used without further purification. Sodium hydride used was previously washed with hexanes, dried *in vacuo* prior to use. Enyne **1a-1g** prepared analogously to known literature procedures.[1] IPr, SIPr, IMes, and I^{t}Bu ligands were prepared as previously reported.[2] The compounds 1-bromo-2-methylbutyne was prepared from the corresponding alcohols.[3] Allyl bromide, 3-bromoprop-1-yne, (3-bromoprop-1-ynyl)trimethylsilane, tetraethyl 1,1,2,2-ethanetetracarboxylate, and isocyanates **2a-2j** were purchased from Sigma Aldrich Chemicals.

All isocyanates were dried over calcium hydride and distilled under freeze-pump-thaw technique. ^{1}H, ^{13}C, nOe, and HMBC nuclear magnetic resonance spectra of pure compounds were acquired at 300, 400, and 500 MHz instruments. All spectras were carried out using $CDCl_3$ and C_6D_6 as the solvent purchased from Cambridge Isotope Labs. Inc. All spectras are referenced to a singlet of chloroform at 7.27 ppm for ^{1}H and to the center line of a triplet at 77.26 ppm for ^{13}C or 7.16 ppm for ^{1}H and 126.80 ppm for ^{13}C unless specified otherwise. The abbreviations s, d, dd, dt, dq, t, td, tq, q, qt, quint, sept, septd, septt, m, brm, brd, brt, and brs stand for singlet, doublet, doublet of doublets, doublet of triplets, doublet of quartets, triplet,

triplet of doublets, triplet of quartets, quartet, quartet of triplets, quintet, septet, septet of doublets, septet of triplets, multiplet, broad multiplet, broad doublet, broad triplets, and broad singlet, in that order. All ^{13}C NMR spectra were proton decoupled. (*E*-), (*Z*-) geometry of the dieneamides was confirmed by nOe experiments (nuclear Overhauser effect). IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer using a NaCl crystal.

Gas Chromatography were performed on an Agilent 6890 instrument with a 30 meter HP-5 column using the following conditions: initial oven temperature: 100 ºC; temperature ramp rate 25 ºC/min.; final temperature: 300 ºC held for 7 minutes; detector temperature: 250 ºC.

Preparation of tetraethylpent-4-ene-1,1,2,2-tetracarboxylate (14)



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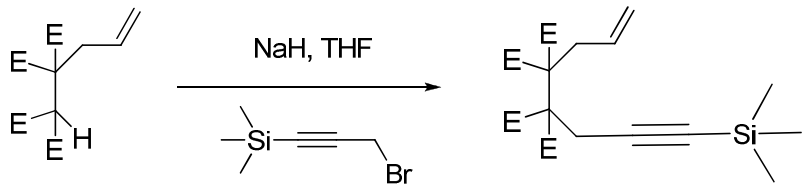
To a stirring suspension of NaH (0.415 mg, 17.277 mmol) in 150 ml THF was added tetraethyl 1,1,2,2-ethanetetracarboxylate (5.0 g, 15.707 mmol) under N_2 counter-flow in two portions. The resulting solution was stirred at room temperature for 1 h after which time allyl bromide (2.1 g, 17.3 mmol) was added. A reflux condenser was attached and the mixture was stirred at reflux for 8 h at which time GC analysis showed no starting ester remained. The solution was cooled to room temperature and quenched with 100 mL of a saturated NH_4Cl solution. The layers were separated and aqueous layer was extracted with Et_2O (3 x 100 mL). The combined organics were washed with brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resulting crude yellow oil was purified by flash column chromatography (10% EtOAc/hexanes then 12% EtOAc/hexanes) to yield **14** (5.3 g, 94%) as a pale yellow oil. The spectral data was compared with the literature values[1].

Preparation of tetraethyl 8-(trimethylsilyl)oct-1-en-7-yne-4,4,5,5-tetracarboxylate (1f):

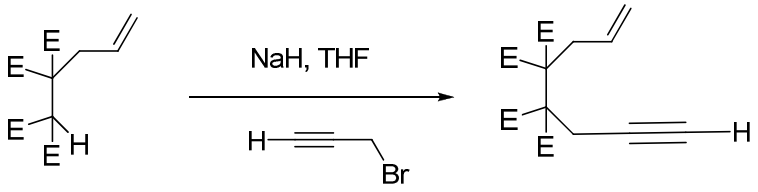


14 **1e**

E= CO_2Et

To a stirring solution of NaH (147 mg, 6.14 mmol) in 20 mL THF, tetraethyl pent-4-ene-1,1,2,2-tetracarboxylate (**14**) in 8 ml THF was added. The resulting mixture was stirred at room temperature for 1 hour. To this reaction mixture was added (3-bromoprop-1-ynyl)trimethylsilane (1.17 g, 6.14 mmol) in a single portion. The resulting solution was refluxed for 48 hrs. After checking the completion of the reaction by gas chromatography, the reaction mixture was quenched by the addition of sat.NH_4Cl (10 ml) and H_2O (10 ml). To the reaction mixture Et_2O (20 ml) was added. The layers were separated and the aqueous layer was extracted with Et_2O (3 x 20 mL). All organic layers were combined and washed with brine (10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The resulting crude oil was purified by flash column chromatography eluting with 10% EtOAc/hexanes to yield enyne **1f** as a yellow oil (862 mg, 65.9%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.82-6.13 (m, 1H), 5.05-5.12 (m, 2H), 4.15-4.32 (m, 8H), 3.20 (s, 2H), 2.80 (d, J= 6.9 Hz, 2H), 1.25-1.30 (m, 12H), 0.20 (s, 9H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 169.3, 168.8, 134.0, 119.1, 102.9, 87.1, 62.6, 62.3, 62.1, 61.8, 36.5, 23.7, 14.0, 14.1, 0.1. IR (neat): 3080, 2983, 2906, 2182, 1737, 1639, 1445, 1390, 1367, 1207, 1033, 920, 847 cm-^{1}. **HRMS** calculated *m/z* for $C_{23}H_{36}O_8NaSi$ (M^+Na) 491.2077, found 491.2071.

Preparation of tetraethyl-oct-1-en-7-yne-4,4,5,5-tetracarboxylate (1f)



14 **1f**

E=CO_2Et

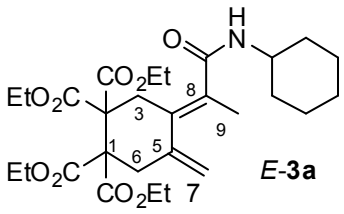
To a stirring solution of NaH (294 mg, 12.28 mmol) in 50 mL THF was added compound (**A**) (2.0 gms, 5.58 mmol). The reaction mixture was stirred for 1 hour after which 3-bromoprop-1-yne (1.46 g, 12.28 mmol) as an 80 % w/v solution in toluene in a single portion. The resulting mixture was refluxed for 24 hrs. After checking the completion of the reaction by gas

chromatography, the reaction mixture was quenched by the addition of sat NH_4Cl (20 mL) and H_2O (20 mL). To the reaction mixture Et_2O (20 mL) was added. The layers were separated and the aqueous layer was extracted with Et_2O (3 x 20 mL). All organic layers were combined and washed with brine (20 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The resulting crude oil was purified by flash column chromatography eluting with 30% ethyl acetate/hexanes to yield enyne **1f** as a colorless solid (1.789 g, 80.95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.81-6.11 (m, 1H), 5.05-5.20 (m, 2H), 4.15-4.30 (m, 8H), 3.15 (d, *J*= 2.4 Hz, 2H), 2.81 (d, *J*= 7.2 Hz, 2H), 2.07 (t, *J*= 2.7 Hz, 1H), 1.20-1.40 (m, 12H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 169.1, 168.8, 133.8, 119.4, 80.2, 70.8, 62.1, 62.0, 61.9, 36.4, 22.4, 14.0. IR (neat): 3277, 3080, 2984, 2906, 1736, 1639, 1445, 1390, 1367, 1209, 1035, 864 cm^{-1}. **HRMS** calculated *m/z* for $C_{20}H_{28}O_8Na$ (M^+Na) 419.1682, found 419.1684

General Cycloaddition Procedure 1:

In the glove box, the enyne and isocyanate in toluene was added to an oven dried scintillation vial equipped with a magnetic stir bar and dissolved. To this reaction mixture, a solution of $Ni(COD)_2$ and IPr which was previously equilibrated for at least 4 hrs was added using a calibrated microsyringe. The reaction mixture was stirred at room temperature or heated in an oil-bath at the desired temperature until the reaction was complete. The consumption of starting material was monitored by GC. The mixture was concentrated *in vacuo* and purified by silica gel column chromatography.

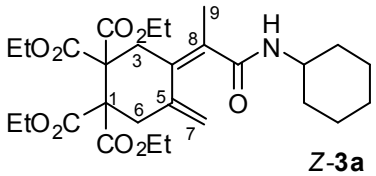
Compounds (*Z*) and (*E*)-tetraethyl-4-(1-(cycloamino)-1-oxopropan-2-ylidene)-5-methylenecyclohexane-1,1,2,2-tetracarboxylate (*Z*/*E*-3a): General procedure **1** was used with enyne **1a** (100 mg, 0.24 mmol), cyclohexyl isocyanate (30.50 mg, 0.24 mmol) **2a**, $Ni(COD)_2$ (6.77 mg, 0.024 mmol), IPr (18.9 mg, 0.048 mmol) and 2.4 ml toluene and stirred for 1 hour at room temperature. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compound ***E*-3a** as a colorless solid (m.p. 130-132 °C) and compound ***Z*-3a** as an oil (90.3 mg, 70%).



E-3a

***E*-3a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.82 (d, *J*=8.8 Hz, 1H), 5.35 (s, 1H), 4.90 (s, 1H), 4.2 (m, 8H), 3.80-3.85 (brm, 1H), 3.05 (d, *J*= 6 Hz, 4H), 1.98 (s, 3H), 1.9-1.1 (brm, 10H), 1.2-1.3 (q, *J*= 5.2, 5.2 Hz, 12H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 170.8, 169.7, 169.2, 139.7, 131.6, 130.5, 116.8, 61.9, 61.8, 60.7, 58.8, 47.8,

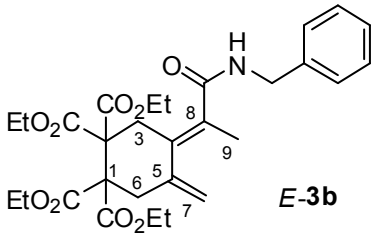
39.7, 35.4, 33.2, 25.7, 24.9, 17.7, 14.1, 13.9. IR (neat): 3608, 3583, 2983, 2933, 2260, 1740, 1262, 1207 cm^{-1}. nOe correlation was seen with a proton on C-7 and the methyl protons on C-9. **HRMS** calculated *m/z* for $C_{28}H_{41}NO_9Na$ (M^+Na) 558.2679, found 558.2670.



Z-**3a**

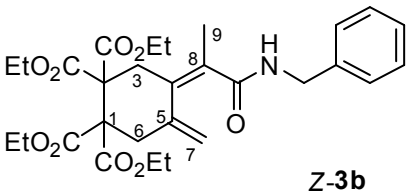
***Z*-3a:** ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.6 (m, 2H), 4.1-4.2 (m, 8H), 3.6-3.8 (s, 1H), 3.20 (s, 2H), 2.90 (s, 2H),1.90 (s, 3H), 1.5-1.75 (m, 6H), 1.05-1.20 (m, 16H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ (ppm) 171.6, 169.5, 169.4, 141.0, 133.6, 131.5, 116.6, 62.1, 61.9, 60.9, 58.8, 47.7, 39.0, 33.4, 32.5, 30.5, 29.9, 25.8, 24.9, 16.0, 14.1, 14.0. IR (neat): 3583, 3392, 2984, 2933, 2855, 2253, 1730, 1656, 1267, 912 cm^{-1}. nOe correlation was seen with vinylic proton on C-7 and methylene protons on C-6. **HRMS** calculated *m/z* for $C_{28}H_{41}NO_9Na$ (M^+Na) 558.2679, found 558.2673.

Compounds (*Z*) and (*E*)-tetraethyl 4-(1-(benzylamino)-1-oxopropan-2-ylidene)-5-methylenecyclohexane-1,1,2,2-tetracarboxylate (*E*/*Z*-3b): General procedure **1** was used with enyne **1a** (100 mg, 0.24 mmol), benzyl isocyanate (32.44 mg, 0.24 mmol) **2b**, $Ni(COD)_2$ (6.77 mg, 0.024 mmol), IPr (18.9 mg, 0.048 mmol) and 2.4 ml toluene and stirred for 2 hours at room temperature. The crude compound was purified by flash chromatography eluting with 30% EtOAc to yield compound ***E*-3b** as a colorless solid (m.p. 95-98 °C) and compound ***Z*-3b** as an oil (90mg, 68%).



E-**3b**

***E*-3b:** ^1H NMR (300 MHz, $CDCl_3$): δ (ppm)7.20-7.40 (m, 5H), 5.92 (t, *J*= 6.3 Hz, 1H), 5.0 (s, 1H), 4.71 (d, *J*= 1.2 Hz, 1H), 4.34 (d, *J*= 5.7 Hz, 2H), 4.25-4.13 (m, 8H), 3.05 (s, 2H), 2.84 (s, 2H), 1.94 (s, 3H), 1.15-1.25 (m, 12H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$): δ (ppm) 172.4, 169.4, 169.3, 140.9, 138.2, 134.2, 130.8, 128.7, 128.1, 127.5, 116.6, 62.1, 61.9, 60.8, 58.7, 43.9, 38.9, 33.5, 16.1, 14.1, 14.0. IR (neat): 3396, 2983, 1735, 1659, 1266, 1204, 864 cm^{-1}. nOe correlation was seen with a proton on C-7 and the protons on C-9. **HRMS** calculated for *m/z* $C_{29}H_{37}NO_9Na$ (M^+Na) 566.2366, found 566.2360.

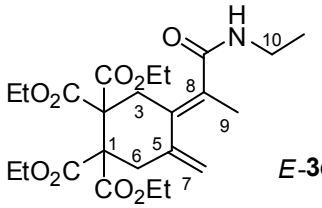


Z-**3b**

***Z*-3b:** ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.29-7.25 (brm, 5H), 6.26 (t, *J*= 5.4 Hz, 1H), 5.12 (m, H), 4.94 (d, *J*= 1.8 Hz, 1H), 4.54 (d, *J*= 6.3 Hz, 2H), 3.8-4.2 (brm, 8H), 2.98 (d, *J*=

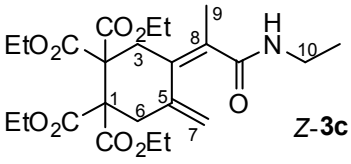
15.9 Hz, 4H), 1.98 (s, 3H), 1.25-1.05 (m, 12 H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 171.6, 169.7, 169.2, 139.8, 138.4, 132.3, 129.6, 128.8, 128.1, 127.6, 116.9, 61.9, 61.9, 60.8, 58.8, 43.6, 39.6, 35.7, 14.0, 13.8. IR (neat): 3396, 2983, 1735, 1659, 1266, 1204, 1041, 912 cm^{-1}. nOe correlation was seen with vinylic proton on C-7 and methylene protons on C-6. **HRMS** calculated for *m/z* $C_{29}H_{37}NO_9Na$ (M^+Na) 566.2366, found 566.2369.

Compounds (*Z*) and (*E*)-tetraethyl 4-(1-(ethylamino)-1-oxopropan-2-ylidene)-5-methylenecyclohexane-1,1,2,2-tetracarboxylate (*Z*/*E*-3c): General procedure **1** was used with enyne **1a** (100 mg, 0.24 mmol), ethyl isocyanate (17.31 mg, 0.24 mmol) **2c**, $Ni(COD)_2$ (6.77 mg, 0.024 mmol), IPr (18.9 mg, 0.048 mmol) and 2.4 ml toluene and stirred for 2 hours 80 °C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compound ***E*-3c** as a colorless solid (m.p. 98-100 °C) and compound ***Z*-3c** as an oil (93.7 mg, 80%).



E-3c

***E*-3c:** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.59 (brs, 1H), 5.10 (s, 1H), 4.90 (s, 1H), 4.18-4.28 (m, 8H), 3.21 (q, J = 6.4 Hz, 2H), 2.89 (s, 4H), 1.60 (d, J = 6.4 Hz, 3H), 1.15-1.25 (m, 12H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 171.7, 169.8, 169.3, 139.6, 131.8, 130.4, 117.0, 62.0, 60.7, 58.9, 39.6, 35.5, 34.2, 17.8, 14.9, 14.1, 13.9. IR(neat):3609, 3584, 2982, 1738, 1647, 1367, 1263, 1209, 1042, 864 cm^{-1}. nOe correlation was seen with a proton on C-7 and the methyl protons on C-9. **HRMS** *m/z* calculated for $C_{24}H_{35}NO_9Na$ (M^+Na) 504.2210, found 504.2209.

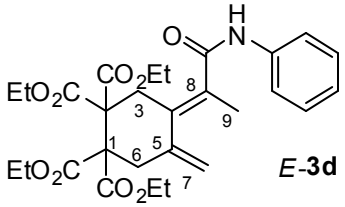


Z-3c

***Z*-3c:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.59 (t, J= 5.6 Hz, 2H), 5.10 (brs, 1H), 4.90 (brs, 1H), 4.15-4.24 (m, 8H), 3.21 (q, J= 6.6 Hz, 2H) 3.14 (s, 2H), 2.84 (s, 2H), 1.84 (s, 3H), 1.26 (m, 12H), 1.06 (t, J= 7.2, 7.2 Hz, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 172.5, 169.5, 169.4, 141.0. 133.8, 131.2, 116.4, 61.8, 61.7, 58.5, 55.9, 31.4, 14.0, 12.9, 3.8. IR (neat): 3584, 3402, 2982, 1735, 1519, 1266, 913 cm^{-1}. nOe correlation was seen with vinylic proton on C-7 and methylene protons on C-6. **HRMS** *m/z* calculated for $C_{28}H_{41}NO_9Na$ (M^+Na) 504.2210, found 504.2207.

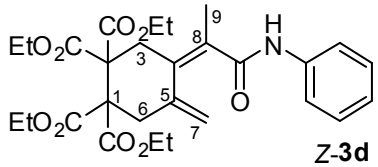
Compounds (*Z*) and (*E*)-tetraethyl- 4-methylene-5-(1-oxo-1-(phenylamino)propan-2-ylidene)cyclohexane-1,1,2,2-tetracarboxylate (3d): General procedure **1** was used with enyne

1a (100 mg, 0.24 mmol), phenylisocyanate (29.10 mg, 0.24 mmol) **2d**, $Ni(COD)_2$ (6.77 mg, 0.024 mmol), IPr (18.9 mg, 0.048 mmol) and 2.4 ml toluene and stirred for 2 hours at 60 °C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compound ***E*-3d** and compound ***Z*-3d** as oils (105.5 mg, 79%).



E-3d

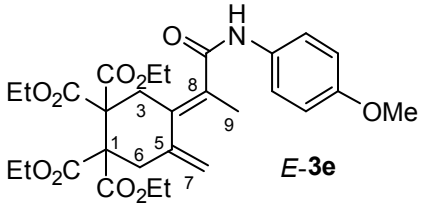
***E*-3d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm). 8.105 (s, 1H), 7.5 (d, *J*= 7.6 Hz, 2H), 7.33 (t, *J*= 6,Hz, 2H), 7.13 (t, *J*=5.4 Hz, 1H), 5.20 (s, 1H), 4.99 (s, 1H), 4.15-4.26 (m, 8H), 3.158 (s, 2H), 2.99 (m,2H), 2.07 (s, 3H), 1.15-1.4 (m, 12H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 169.9, 169.2, 139.5, 138.3, 132.2, 130.5, 129.2, 124.3, 119.8, 117.3, 62.2, 62.1, 60.4, 59.3, 39.8, 35.6, 18.1, 14.1, 13.9. IR (neat): 3348, 2984, 1738, 1673, 1532, 1441, 1266, 1041, 915, 732 cm^{-1}. nOe correlation was seen with a proton on C-7 and the methyl protons on C-9. **HRMS** calculated *m/z* for $C_{28}H_{35}NO_9Na$ (M^+Na) 552.2210, found 552.2205.



Z-3d

***Z*-3d**: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55 (s, 1H), 7.48 (d, *J*= 8Hz, 2H), 7.31 (t, *J*= 7.6Hz, 2H), 7.09 (t, *J*= 4.1Hz, 1H), 5.20 (s, 1H), 4.99 (s, 1H), 4.25 (m, 8H), 3.23 (s, 2H), 2.89 (s, 2H), 1.95 (s, 3H), 1.42-1.28 (m, 12H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 170.6, 169.5, 169.4, 141.2, 138.7, 135.3, 131.4, 129.1, 124.2, 119.8, 117.1, 62.2, 62.1, 60.9, 58.6, 38.7, 33.5, 15.9, 14.1, 14.0. IR (neat): 3365, 2984, 1739, 1681, 1598, 1440, 1267, 1043, 915 cm^{-1}. nOe correlation was seen with vinylic proton on C-7 and methylene protons on C-6. **HRMS** calculated for *m/z* $C_{28}H_{35}NO_9Na$ (M^+Na) 552.2210, found 558.2208.

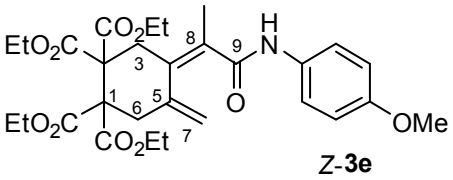
Compounds (*Z*) and (*E*)-tetraethyl 4-(1-(4-methoxyphenylamino)-1-oxopropan-2-ylidene)-5-methylenecyclohexane-1,1,2,2-tetracarboxylate (*Z*/*E*-3e). General procedure **1** was used with enyne **1a** (100 mg, 0.24 mmol), p-methoxyphenyl isocyanate (36.33 mg, 0.24 mmol) **2e**, $Ni(COD)_2$ (6.77 mg, 0.024 mmol), IPr (18.9 mg, 0.048 mmol) and 2.4 ml toluene and stirred for 2 hours at 60° C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compound ***E*-3e** as a colorless solid (m.p. 119-120 °C) and compound ***Z*-3e** as an oil (101.7 mg, 74%).



E-3e

***E*-3e:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96 (s, 1H), 7.48 (d, *J*= 8.8 Hz, 2H), 6.87 (d, *J*= 8.8 Hz, 2H), 5.19 (s, 1H), 4.99

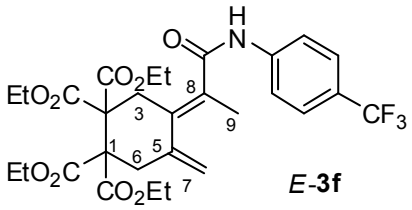
(s, 1H), 4.05-4.20 (m, 8H), 3.80 (s, 3H), 3.15 (s, 2H), 2.99 (s, 2H), 2.07(s, 3H), 1.05-1.25 (m, 12H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 169.9, 169.7, 169.2, 156.6, 139.7, 132.3, 131.4, 130.6, 121.7, 117.2, 114.4, 62.2, 62.0, 60.5, 59.4, 55.7, 39.9, 35.7, 18.0, 14.1, 13.9. IR (neat): 3351, 2984, 2253, 1739, 1513, 1248, 1038 cm^{-1}. nOe correlation was seen with a proton on C-7 and the methyl protons on C-9. **HRMS** calculated for *m/z* $C_{29}H_{37}NO_{10}Na$ ($M^{+}Na$) 582.2315, found 582.2314.



Z-**3e**

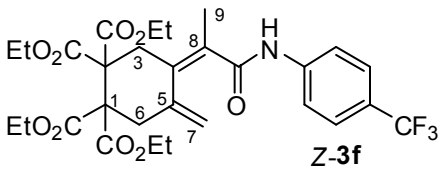
***Z*-3e:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42 (s, 1H), 7.38 (d, *J*= 9.2 Hz, 2H), 6.85 (d, *J*= 9.2 Hz, 2H), 5.16 (s, 1H), 4.94 (s, 1H), 4.05-4.24 (m, 8H), 3.79 (s, 3H), 3.23 (s, 2H), 2.88 (s, 2H), 1.94 (s, 3H), 1.20-1.28 (m, 12H) . ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 170.5, 169.5, 169.4, 156.7, 141.3, 135.1, 131.9, 131.5, 121.7, 116.9, 114.4, 62.2, 62.1, 61.1, 58.7, 55.7, 38.8, 33.6, 29.9, 16.0, 14.1, 14.0. IR (neat): 3372, 2985, 2937, 2253, 1729, 1513, 1268, 911 cm^{-1}. nOe correlation was seen with vinylic proton on C-7 and methylene protons on C-6. **HRMS** calculated for *m/z* $C_{29}H_{37}NO_{10}Na$ ($M^{+}Na$) 582.2315, found 582.2313.

Compounds (*Z*) and (*E*)-tetraethyl 4-methylene-5-(1-oxo-1-(4-(trifluoromethyl)phenylamino)propan-2-ylidene)cyclohexane-1,1,2,2-tetracarboxylate (*Z*/*E*-3f): General procedure **1** was used with enyne **1a** (100 mg, 0.24 mmol), 4-trifluoromethylphenyl isocyanate (36.33 mg, 0.24 mmol) **2f**, $Ni(COD)_2$ (6.77 mg, 0.024 mmol), IPr (18.9 mg, 0.048 mmol) and 2.4 ml toluene and stirred for 7 hours at 100° C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compound ***E*-3f** and compound ***Z*-3f** as oils (83.2 mg, 57%).



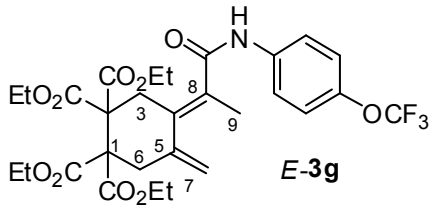
E-**3f**

***E*-3f:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.52 (s, 1H), 7.72 (d, *J*= 8.8 Hz, 2H), 7.58 (d, *J*=8.8 Hz, 2H), 5.22 (s, 1H), 5.01 (s, 1H), 4.15-4.21 (m, 8H), 3.16 (s, 2H), 2.95 (s, 2H), 2.08 (s, 3H), 1.15-1.40 (m, 12H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 170.2, 169.9, 169.1, 141.5, 139.4, 132.8, 130.2, 126.5, 126.5, 119.4, 117.6, 62.4, 62.1, 60.3, 59.6, 39.9, 35.7, 18.1, 14.1, 13.9. IR (neat): 3339, 2985, 2940, 2257, 1737, 1684, 1368, 1262 cm^{-1}. **HRMS** calculated for *m/z* $C_{28}H_{41}NO_9Na$ ($M^{+}Na$) 620.2083, found 620.2079.



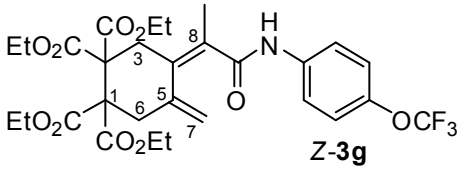
***Z*-3f:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm). 7.79 (s, 1H), 7.59 (m, 4H), 5.14 (s, 1H), 4.93 (s, 1H), 4.15-4.25 (m, 8H), 3.24 (s, 2H), 2.88 (s, 2H), 1.94 (s, 3H), 1.29 (m, 12H). ^{13}C $\{^{1}$H$\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 170.9, 169.5, 169.3, 141.9, 141.4, 136.3, 126.4, 126.4, 119.4, 119.3, 117.4, 62.3, 62.2, 61.1, 58.6, 38.6, 33.6, 15.9, 14.1, 14.0. IR (neat): 3356, 2986, 1739, 1692, 1324, 1266, 1117, 919 cm^{-1}. nOe correlation was seen with vinylic proton on C-7 and methylene protons on C-6. **HRMS** calculated for *m/z* $C_{28}H_{41}NO_9Na$ (M^+Na) 620.2083, found 620.2079.

Compounds (*Z*) and (*E*)-tetraethyl 4-methylene-5-(1-oxo-1-(4-(trifluoromethoxy)phenylamino)propan-2-ylidene)cyclohexane-1,1,2,2-tetracarboxylate (*Z*/*E*-3g). General procedure **1** was used with enyne **1a** (100 mg, 0.24 mmol), 4-(trifluoromethoxy)phenyl isocyanate (49.48 mg, 0.24 mmol) **2g**, $Ni(COD)_2$ (6.77 mg, 0.024 mmol), IPr (18.9 mg, 0.048 mmol) and 2.4 ml toluene and stirred for 5 hours at 80° C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compound ***E*-3g** and compound ***Z*-3g** as oils (99.8 mg, 66.7%).



E-3g

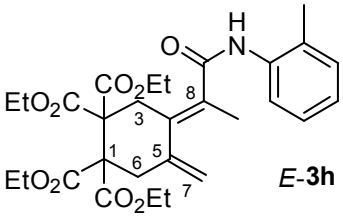
***E*-3g:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.36 (s, 1H), 7.61 (d, *J*= 12.4 Hz, 2H), 7.17 (d, *J*= 10.8 Hz, 2H), 5.19 (s, 1H), 4.98 (s, 1H), 4.18 (m, 8H), 3.14 (s, 2H), 2.96 (s, 2H), 2.05 (s, 3H), 1.24 (m, 12H). ^{13}C $\{^{1}$H$\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 169.9, 169.1, 145.4, 139.5, 137.1, 132.7, 130.3, 126.49, 121.9, 121.0, 117.4, 62.3, 62.1, 60.3, 59.6, 39.9, 35.7, 18.0, 14.1, 13.9. IR (neat): 3339, 2985, 2874, 1738, 1265, 1203, 1058, 918 cm^{-1}. **HRMS** calculated for *m/z* $C_{28}H_{41}NO_9Na$ (M^+Na) 636.2033, found 636.2027.



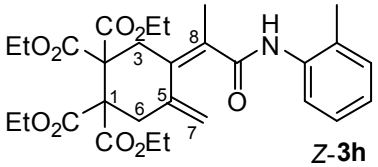
Z-3g

***Z*-3g:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.67(s, 1H), 7.51 (d, *J*= 9.2 Hz, 2H), 7.16 (d, *J*= 8.4 Hz, 2H), 5.14 (s, 1H), 4.94 (s, 1H), 4.05-4.25 (m, 8H), 3.24 (s, 2H), 2.88 (s, 2H), 1.93 (s, 3H) 1.05- 1.29 (m, 12H). ^{13}C $\{^{1}$H$\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 170.8, 169.5, 169.3, 145.3, 141.4, 137.4, 135.9, 131.2, 121.9, 120.9, 117.2, 62.3, 62.1, 61.1, 58.6, 38.7, 33.5, 15.9, 14.1, 14.0. IR (neat): 3358, 2985, 2940, 2255, 1738, 1682, 1512, 1265, 1200, 1107, 1043, 919, 861 cm^{-1}. nOe correlation was seen with the other vinylic proton on C-7. **HRMS** calculated for *m/z* $C_{28}H_{41}NO_9Na$ (M^+Na) 636.2033, found 636.2031.

Compounds (*Z*) and (*E*)-tetraethyl 4-methylene-5-(1-oxo-1-(o-tolylamino)propan-2-ylidene)-cyclohexane-1,1,2,2-tetracarboxylate (*Z*/*E*-3h). General procedure **1** was used with enyne **1a** (100 mg, 0.24 mmol), 2-methylphenyl isocyanate (32.43 mg, 0.24 mmol) **2h**, $Ni(COD)_2$ (6.77 mg, 0.024 mmol), IPr (18.9 mg, 0.048 mmol) and 2.4 ml toluene and stirred for 1 hour at 80° C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/ hexanes to yield compounds ***E*-3h** and ***Z*-3h** as an inseparable mixture of isomers as an oil (94 mg, 71%).



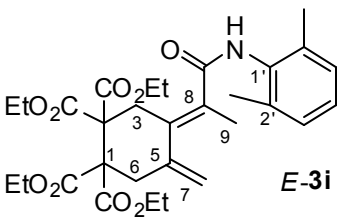
E-3h



Z-3h

***E*-3h** and ***Z*-3h:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J*=7.2 Hz, 2H), 7.76 (d, *J*= 7.8 Hz, 2H), 7.60 (s, 1H), 7.44 (s, 2H), 7.23-7.08 (m, 6H), 7.03 (q, *J*= 4.8, 4.8 Hz, 2H), 5.22-5.19 (m, 3H), 4.99 (d, *J*= 2.1 Hz, 1H), 4.94 (d, *J*= 1.5 Hz, 2H), 4.28-4.09 (m, 16H), 3.21 (appd, 6H), 3.02 (s, 2H), 2.88 (s, 4H), 2.27 (d, *J*= 11.4 Hz, 8H), 2.097 (s, 3H), 1.95 (s, 6H), 1.31-1.71 (m, 24H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 170.6, 170.1, 169.7, 169.3, 169.3, 169.2, 141.1, 139.5, 136.4, 135.6, 134.7, 132.4, 131.4, 130.7, 130.5, 130.3, 130.2, 128.2, 126.8, 125.6, 124.6, 123.8, 121.1, 117.3, 62.2, 62.0, 61.9, 60.9, 60.5, 59.0, 58.5, 39.7, 38.9, 35.7, 33.4, 18.1, 17.7, 16.1, 14.0, 13.9, 13.8. IR (neat): 3386, 2983, 2939, 2906, 2248, 1726, 1682, 1517, 1268, 1200, 1096, 1057, 1044, 919, 863, 702 cm^{-1}. HRMS *m/z* calculated for $C_{28}H_{41}NO_9Na$ (M^+Na) 566.2366, found 566.2368.

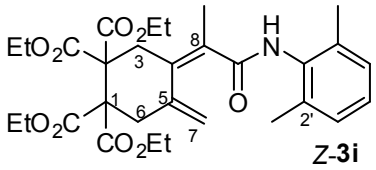
Compounds (*Z*) and (*E*)-tetraethyl 4-(1-(2,6-dimethylphenylamino)-1-oxopropan-2-ylidene)-5-methylenecyclohexane-1,1,2,2-tetracarboxylate (*Z*/*E*-3i). General procedure **1** was used with enyne **1a** (100 mg, 0.24 mmol), 2,6-dimethylphenyl isocyanate (35.85 mg, 0.24 mmol) **2i**, $Ni(COD)_2$ (6.77 mg, 0.024 mmol), IPr (18.9 mg, 0.048 mmol) and 2.4 ml toluene and stirred for 1.5 hours at 80° C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compound ***E*-3i** as a colorless solid (m.p. 138-140 °C) and compound ***Z*-3i** as oil (109 mg, 80%).



E-3i

***E*-3i:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33 (brs, 1H), 7.09 (brs, 3H), 5.20 (s, 1H), 4.99 (d, *J*= 1.2 Hz, 1H), 4.18-4.25 (m, 8H), 3.28 (s, 2H), 3.06 (s, 2H), 2.28 (s, 6H), 2.14 (s, 3H), 1.20-1.24 (m, 12H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 170.4, 169.8, 169.3,

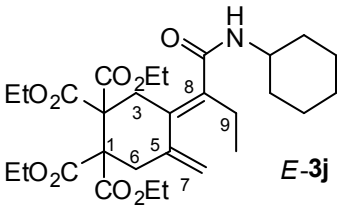
139.6, 135.8, 133.7, 132.2, 130.1, 128.5, 127.5, 117.2, 62.1, 60.8, 59.1, 39.8, 36.1, 19.0, 18.3, 14.1, 13.9. IR (neat): 3354, 2983, 2240, 1739, 1270, 1041 cm^{-1}. **HRMS** calculated for *m/z* $C_{30}H_{39}NO_9Na$ (M^+Na) 580.2523, found 580.2515.



Z-**3i**

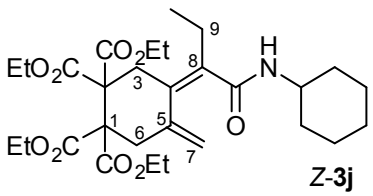
***Z*-3i:** ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.22 (s, 1H), 7.06 (brs, 3H), 5.32 (s, 1H), 5.029 (s, 1H), 4.15- 4.23 (m, 8H), 3.29 (s, 2H), 2.90 (s, 2H), 2.23 (s, 6H), 1.98 (s, 3H), 1.15-1.30 (m, 12H). ^{13}C {^1H} NMR (100 MHz, $CDCl_3$): δ (ppm) 170.8, 169.5, 169.4, 141.5, 135.8, 133.9, 133.6, 130.9, 128.6, 127.6, 117.9, 62.24, 62.0, 61.2, 58.7, 39.0, 33.6, 18.7, 16.5, 14.1, 14.0. IR (neat): 3368, 2982, 2360, 1738, 1266, 1041 cm^{-1}. nOe correlation was seen between the vinylic protons on C-7. **HRMS** *m/z* calculated for $C_{28}H_{41}NO_9Na$ (M^+Na) 580.2523, found 580.2515.

Compounds (*Z*) and (*E*)-tetraethyl 4-(1-(cyclohexylamino)-1-oxobutan-2-ylidene)-5-methylenecyclohexane-1,1,2,2-tetracarboxylate (*Z*/*E*-3j): General procedure **1** was used with enyne **1b** (100 mg, 0.23 mmol), cyclohexylisocyanate (29.48 mg, 0.23 mmol) **2a**, $Ni(COD)_2$ (6.77 mg, 0.023 mmol), IPr (18.9 mg, 0.046 mmol) and 2.3 ml toluene and stirred for 4 hours at room temperature. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compounds ***E*-3j** as a colorless solid (m.p. 88-90 °C) and ***Z*-3j** as an oil (115.9 mg, 89.5%).



E-**3j**

***E*-3j:** ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.81 (d, *J*= 8.7 Hz, 1H), 5.06 (s, 1H), 4.93 (d, *J*= 1.8 Hz, 1H), 4.20 (m, 8H), 3.80-3.91 (m, 1H), 3.0 (d, *J*= 7.2 Hz, 4H), 2.43 (q, *J*= 7.5 Hz, 2H), 1.90-1.95 (m, 2H)), 1.6-1.8 (m, 4H), 1.58-1.05 (m, 12H), 0.99 (t, *J*= 7.2, 3H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$): δ (ppm) 169.8, 169.8, 169.3, 139.9, 136.8, 131.2, 116.1, 62.0, 61.9, 61.0, 58.8, 47.9, 39.8, 35.7, 33.3, 30.5, 29.8, 25.8, 25.0, 24.1, 14.1, 13.9, 13.5. IR (neat): 3385, 3068, 2982, 2253, 1727, 1641, 1268, 1206, 912 cm^{-1}. nOe correlation was seen between a vinylic proton on C-7 and the protons of the ethyl group on C-8. **HRMS** *m/z* calculated for $C_{29}H_{43}NO_9Na$ (M^+Na) 572.2836, found 572.2831.

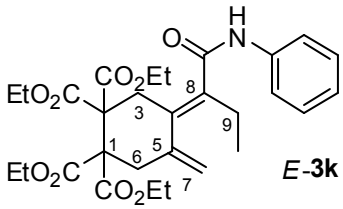


Z-**3j**

***Z*-3j:** ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.61 (d, *J*= 8.7 Hz, 1H), 5.16 (s, 1H), 4.89 (s, 1H), 4.12-4.30 (m, 8H), 3.71-3.80 (brm, 1H), 3.19 (s, 2H), 2.80 (s, 2H), 2.27 (q, *J*= 5.7 Hz, 2H), 1.7-

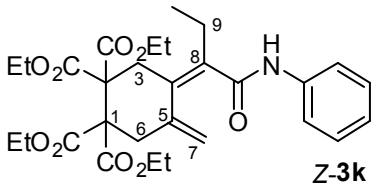
1.85 (m, 2H), 1.5-1.72 (m, 4H), 1.20-1.0 (m, 16H), 0.941 (t, *J*=7.5 Hz, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 170.9, 169.5, 141.2, 137.8, 133.1, 116.6, 62.2, 61.9, 61.2, 58.6, 47.6, 38.8, 33.1, 32.6, 25.8, 24.9, 23.0, 14.1, 12.8. IR (neat): 3394, 3087, 2981, 2856, 2253, 1730, 1640, 1267, 913 cm^{-1}. nOe correlation was seen between the vinylic protons on C-7. **HRMS** *m/z* calculated for $C_{29}H_{43}NO_9Na$ (M^+Na) 572.2836, found 572.2834

Compounds (*Z*) and (*E*)-tetraethyl 4-methylene-5-(1-oxo-1-(phenylamino)butan-2-ylidene)cyclohexane-1,1,2,2-tetracarboxylate (*Z*/*E*-10k). General procedure **1** was used with enyne **1b** (100 mg, 0.23 mmol), phenyl isocyanate (28.13 mg, 0.23 mmol) **2b**, $Ni(COD)_2$ (6.77 mg, 0.023 mmol), IPr (18.9 mg, 0.046 mmol) and 2.3 ml toluene and stirred for 6 hours at room temperature. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compound ***E*-3k** and compound ***Z*-3k** as oils (114.6 mg, 89%).



E-3k

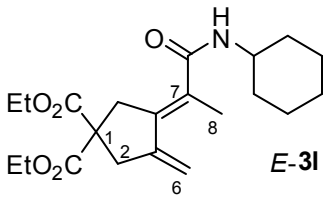
***E*-3k:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98 (s, 1H), 7.58 (d, *J*= 7.6 Hz, 1H), 7.34 (t, *J*= 7.6 Hz, 2H), 7.12 (t, *J*= 7.6, 7.2 Hz, 1H), 5.13 (s, 1H), 5.01 (s, 1H), 4.15-4.24 (m, 8H), 3.13 (s, 2H), 3.02 (s, 2H), 2.54 (q, *J*= 7.6 Hz, 2H), 1.09 (s, 3H), 1.19-1.30 (m, 8H), 1.09 (t, *J*= 7.6 Hz, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 169.9, 169.2, 139.9, 138.2, 136.9, 132.0, 129.2, 124.4, 120.0, 116.4, 62.2, 62.1, 60.8, 59.4, 40.0, 36.1, 30.5, 29.9, 24.6, 14.1, 13.9, 13.7. IR (neat): 3370, 2983, 2937, 2253, 1727, 1656, 1270, 1200, 912, 733 cm^{-1}. nOe correlation was seen between a vinylic proton on C-7 and the protons of the ethyl group on C-8. **HRMS** *m/z* calculated for $C_{29}H_{37}NO_9Na$ (M^+Na) 566.2366, found 566.2353.



Z-3k

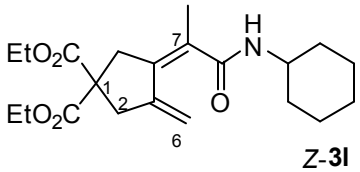
***Z*-3k:** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.63 (s, 1H), 7.50 (d, *J*= 5.4 Hz, 2H), 7.31 (t, *J*= 5.7, 5.7 Hz, 2H), 7.09 (t, *J*= 5.4, 5.4 Hz, 1H), 5.17 (s, 1H), 4.92 (s, 1H), 4.29-4.17 (m, 8H), 3.26 (s, 2H), 2.86 (s, 2H), 2.37 (q, *J*= 5.7 Hz, 2H), 1.25-1.32 (m, 12H), 1.01 (t, *J*= 5.7, 5.4 Hz, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 170.3, 169.5, 169.4, 141.5, 138.8, 137.8, 134.9, 129.1, 124.2, 119.8, 117.2, 62.3, 62.1, 61.3, 58.6, 38.6, 33.2, 23.2, 14.1, 12.9. IR (neat): 3372, 2981, 2935, 1727, 1683, 1269, 1039 cm^{-1}. nOe correlation was seen between the vinylic protons on C-7. **HRMS** *m/z* calculated for $C_{29}H_{37}NO_9Na$ (M^+Na) 566.2366, found 566.2361.

Compounds (*Z*) and (*E*)-diethyl-3-(1-(cyclohexylamino)-1-oxopropan-2-ylidene)-4-methylenecyclopentane-1,1-dicarboxylate (*Z*/*E*-3l): General procedure **1** was used with enyne **1c** (50 mg, 0.2 mmol), cyclohexyl isocyanate (24.80 mg, 0.2 mmol) **2a**, $Ni(COD)_2$ (5.5 mg, 0.02 mmol), IPr (15.5 mg, 0.04 mmol) and 2 ml toluene and stirred for 4 hours at 80 °C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compounds ***E*-3l** and ***Z*-3l** as oils (48.7 mg, 65%).



E-**3l**

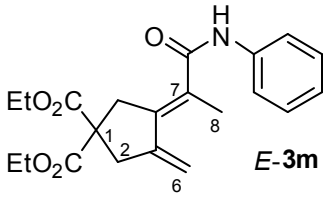
***E*-3l:** ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.86 (d, *J*= 8.1 Hz, 1H), 5.25 (d, *J*= 9.3 Hz, 2H), 4.18 (q, *J*= 7.2 Hz, 4H), 3.76-3.92 (m, 1H), 3.11 (s, 2H), 3.04 (s, 2H), 2.05 (s, 3H), 1.90-2.02 (brm, 2H), 1.56-1.8 (brm, 6H), 1.1-1.4 (m, 8H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$): δ (ppm) 171.4, 170.6, 144.7, 135.9, 129.4, 113.7, 61.9, 57.5, 48.3, 42.2, 40.3, 33.2, 30.5, 29.9, 25.7, 25.1, 17.9, 14.2. IR (neat): 3372, 2982, 2933, 2856, 2244, 1730, 1632, 1524, 1242, 971, 733 cm^{-1}. nOe correlation was seen between a vinylic proton on C-6 and the protons of the ethyl group on C-8. **HRMS** *m/z* calculated for $C_{21}H_{31}NO_5Na$ (M^+Na) 400.2100, found 400.2099.



Z-**3l**

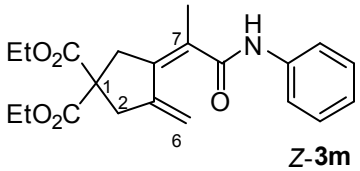
***Z*-3l:** ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.44 (d, *J*= 8.4 Hz, 1H), 5.32 (s, 1H), 5.06 (s, 1H), 4.19 (q, *J*= 7.5 Hz, 4H), 3.70-3.88 (brm,1H), 2.97-3.02 (brs, 3H), 1.92 (s, 3H), 1.8-1.9 (m, 2H)1.57-1.77 (brm, 6H), 1.32-1.10 (m, 8H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$): δ (ppm) 171.4, 170.7, 142.5, 134.3, 128.5, 111.0, 61.9, 57.0, 48.0, 42.4, 39.0, 32.7, 25.7, 25.0, 19.1, 14.2. IR (neat): 3375, 3285, 2981, 2931, 2855, 2361, 1733, 1625, 1247, 1190, 1159, 891, 862 cm^{-1}. **HRMS** *m/z* calculated for $C_{21}H_{31}NO_5Na$ (M^+Na) 400.2100, found 400.2102

Compounds (*Z*) and (*E*)-diethyl-3-methylene-4-(1-oxo-1-(phenylamino)propan-2-ylidene)cyclopentane-1,1-dicarboxylate (*Z*/*E*-3m): General procedure **1** was used with enyne **1c** (50 mg, 0.2 mmol), phenyl isocyanate (23.66 mg, 0.2 mmol) **2b**, $Ni(COD)_2$ (5.5 mg, 0.02 mmol), IPr (15.5 mg, 0.04 mmol) and 2 ml toluene and stirred for 3 hours at 80 °C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compounds ***E*-3m** and ***Z*-3m** both as oils (72 mg, 72%).



E-**3m**

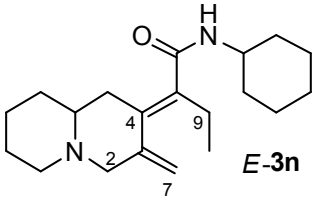
***E*-3m:** ^{1}H NMR (300MHz, $CDCl_3$): δ (ppm) 8.237 (s, 1H), 7.66 (d, *J*= 8.1 Hz, 2H), 7.35 (t, *J*= 7.5 , 8.1 Hz, 2H), 7.15 (s, *J*= 7.8, 7.2 Hz, 1H), 5.34 (s, 2H), 4.21 (q, *J*= 7.2 Hz, 4H), 3.14 (s, 4H), 2.16 (s, 3H), 1.25 (t, *J*= 6.9 Hz, 6H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 171.5, 169.6, 144.2, 138.4, 136.8, 129.4, 129.2, 124.4, 119.9, 114.3, 62.1, 57.4, 41.7, 40.5, 17.8, 14.2. IR (neat): 3299, 2982, 1733, 1654, 1533, 1239, 1074, 904, 861, 757 cm^{-1}. nOe correlation between the vinylic proton on C-6 and the methyl protons on C-7. **HRMS** *m/z* calculated for $C_{21}H_{25}NO_5Na$ (M^+Na) 394.1630, found 394.1642.



Z-**3m**

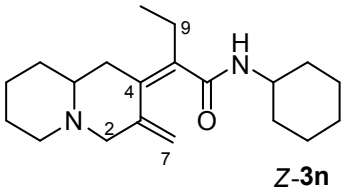
***Z*-3m:** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.52 (d, *J*=8 Hz, 2H), 7.34 (t, *J*=7.6, 8 Hz, 3H), 7.13 (t, *J*= 7.2, 7.6 Hz, 1H), 5.30 (s, 1H), 5.12 (s, 1H), 4.23 (q, *J*= 7.2 Hz, 4H), 3.06 (s, 4H), 2.31 (s, 3H), 1.27 (t, *J*= 7.2 Hz, 6H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 171.3, 169.4, 142.7, 138.2, 136.1, 129.3, 128.3, 124.6, 119.8, 111.9, 62.02, 56.9, 42.3, 39.2, 18.8, 14.2. IR (neat): 3306, 2980, 1731, 1665, 1255, 1194, 1096, 756 cm^{-1}. nOe correlation between the vinylic protons on C-6. **HRMS** *m/z* calculated for $C_{21}H_{25}NO_5Na$ (M^+Na) 394.1630, found 394.1639.

Compounds (*Z*) and (*E*)-*N*-cyclohexyl-2-(2-methylene-1H-quinolizin-3(2H, 4H, 6H, 7H, 8H, 9H, 9aH)-ylidene)butanamide (*Z*/*E*-3n): General procedure **1** was used with enyne **1d** (100 mg, 0.52 mmol), cyclohexylisocyanate (65.47 mg, 0.52 mmol) **2b**, $Ni(COD)_2$ (14.30 mg, 0.052 mmol), IPr (40.38 mg, 0.104 mmol) and 5.2 ml toluene and stirred for 3 hours at 80 °C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compounds ***E*-3n** as a colorless solid (m.p.172-175 °C) and ***Z*-3n** as an oil (131.5 mg, 79%).



E-**3n**

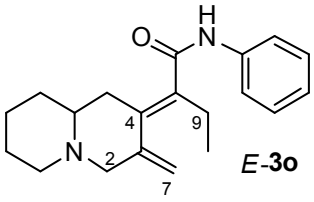
***E*-3n:** ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.76 (m, 1H), 4.98 (s, 1H), 4.79 (s, 1H), 3.85-3.92 (m, 1H), 3.40-3.52 (m, 1H), 2.80-2.85 (m, 1H), 2.57-2.60 (m, 1H), 2.30-2.50 (m, 2H), 2.20-2.25 (m, 1H), 1.93-2.10 (m, 6H), 1.52-1.740 (m, 8H), 1.15-1.43 (m, 6H), 1.01 (t, *J*= 7.6 Hz, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 169.8, 143.8, 134.6, 134.3, 111.9, 63.9, 60.6, 56.1, 48.3, 43.6, 33.4, 32.9, 25.8, 25.7, 25.2, 24.1, 23.9, 13.5. IR (neat): 3372, 2981, 2935, 1727, 1683, 1269, 1039 cm^{-1}. nOe correlation between a vinylic proton on C-7 and the ethyl protons on C-8. **HRMS** *m/z* calculated for $C_{20}H_{33}N_2ONa$ (M^+Na) 317.2593, found 317.2588.



Z-**3n**

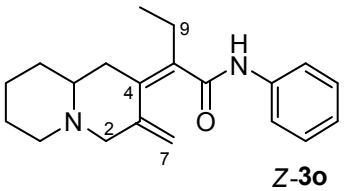
***Z*-3n:** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 5.41-5.39 (m, 1H), 5.05 (s, 1H), 4.80 (s, 1H), 3.60-3.80 (m, 1H), 3.57-3.60 (m, 1H), 3.53 (s, 1H), 2.80-2.92 (m, 1H), 1.8-2.4 (m, 6H), 1.4-1.8 (m, 6H) 0.8-1.4 (m,8H),. ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 170.2,143.6, 135.7, 133.7, 113.1, 63.4, 57.6, 56.4, 47.6, 42.9, 33.3, 33.1, 25.7, 25.6, 24.8, 24.1, 23.4, 13.2. IR (neat): 3372, 2981, 2935, 1727, 1683, 1269, 1039 cm^{-1}. nOe correlation between the vinylic protons on C-7. **HRMS** *m/z* calculated for $C_{20}H_{33}N_2ONa$ (M^+Na) 317.2593, found 317.2593.

Compounds (*Z*) and (*E*)-2-(2-methylene-1H-quinolizin-3(2H,4H,6H,7H,8H,9H,9aH)-ylidene)-N-phenylbutanamide (*Z*/*E*-3o): General procedure **1** was used with enyne **1d** (100 mg, 0.52 mmol), phenyl isocyanate (62.47 mg, 0.52 mmol) **2b**, $Ni(COD)_2$ (14.30 mg, 0.052 mmol), IPr (40.38 mg, 0.104 mmol) and 5.2 ml toluene and stirred for 3 hours at 80 °C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compound ***E*-3o** as a colorless solid (m.p. 98-100 °C) and compound ***Z*-3o** as oil (115.3 mg, 71%).



E-**3o**

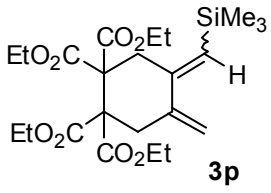
***E*-3o:** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.08 (m, 1H), 7.62 (d, *J*= 5.7 MHz, 2H), 7.20-7.35 (m, 2H), 7.12 (t, *J*= 7.2 Hz, 2H), 5.04 (s, 1H), 4.85 (s, 1H), 3.65-3.70 (m, 1H), 2.9-3.1 (brs, 1H), 2.81 (d, *J*= 11.2 Hz, 1H), 2.66 (d, *J*= 12 Hz, 1H), 2.49-2.58 (m, 2H), 2.31 (m, 1H), 2.01-2.15 (m, 3H), 1.59-1.76 (m, 4H), 1.24 -1.56 (m, 2H), 1.09 (t, *J*= 7.6 Hz, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 169.6, 144.0, 138.5, 129.6, 124.8, 120.4, 112.3, 64.4, 61.0, 56.4, 44.0, 33.3, 26.0, 24.4, 24.4, 14.0. IR (neat): 3275, 2930, 2798, 1672, 1590, 1539, 1250, 735, 690 cm^{-1}. nOe correlation between a vinylic proton on C-7 and the ethyl protons on C-8. **HRMS** *m/z* calculated for $C_{20}H_{27}N_2O$ (M^+Na) 311.2123, found 311.2124.



Z-**3o**

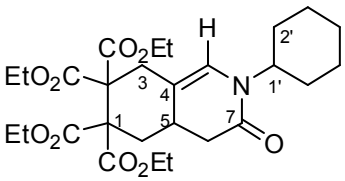
***Z*-3o:** ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.43-7.55 (m, 3H), 7.29 (d, *J*=7.2 Hz, 2H), 7.05-7.09 (m, 1H), 5.06 (t, *J*= 2 Hz, 1H), 4.85 (m, 1H), 3.61 (d, *J*= 12.4 Hz, 1H), 2.95-3.0 (m, 1H), 2.55-2.61 (m, 1H), 1.90-2.46 (m, 4H), 1.45-1.80 (m, 4H), 1.05-1.20 (m, 6H)^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): 169.9, 143.8, 138.6, 135.4, 135.4, 129.1,

124.3, 119.8, 113.4, 63.3, 57.6, 56.4, 42.7, 33.1, 25.7, 24.1, 23.5, 13.4. IR (neat): 3285, 2935, 2798, 1662, 1598, 1539, 1247, 907, 732, 693 cm^{-1}. nOe correlation between the vinylic protons on C-7. **HRMS** *m/z* calculated for $C_{20}H_{27}N_2O$ (M^+Na) 311.2123, found 311.2122.



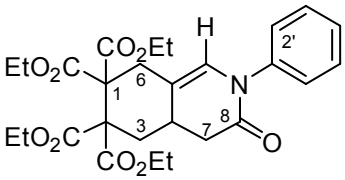
3p

Preparation of (*E*)-tetraethyl-2-butyryl-4-methylene-5-((trimethylsilyl)methylene)cyclohexane)-1,1,2-tricarboxylate (3p): General procedure **1** was used with by stirring enyne **1e** (50 mg, 0.11 mmol) and cyclohexyl isocyanate **2a** (13.35 mg, 0.11 mmol), $Ni(COD)_2$ (3.03 mg, 0.011 mmol), IPr (8.54 mg, 0.022 mmol) for 24 hours at 100 °C. The crude compound was purified by column chromatography eluting with 30% EtOAc/hexanes to yield compound **3p** as an oil (13.8 mg, overall yield= 31%). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.24 (s, 1H), 5.94 (s, 1H), 5.12 (s, 1H), 5.03 (s, 1H), 4.18 (m, 8H), 2.16 (s, 3H), 1.73 (s, 2H), 1.21-1.29 (m, 12H), 0.03 (s, 9H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$): δ (ppm). 169.3, 139.0, 136.8, 120.7, 113.6, 62.0, 61.9, 60.3, 36.3, 29.9, 22.5, 14.0, -0.9 ppm. HRMS m/z calculated for $C_{23}H_{36}O_8NaSi$ (M^+Na) 491.2077, found 491.2071.



10

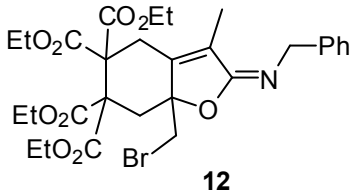
Preparation of tetraethyl-2-cyclohexyl-3-oxo-3,4,4a,5-tetrahydroisoquinoline-6,6,7,7(2H,8H)-tetracarboxylate (10). General procedure 1 was used with enyne **1f** and cyclohexyl isocyanate (31.59 mg, 0.25 mmol)**2a**, Ni(COD)2, IPr and toluene stirring for 4 hours at 80 °C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compound **10** as an oil (9.5 mg, 15%). ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 5.89 (s, 1H), 4.0-4.3 (m, 8H), 3.4-3.6 (m, 1H), 2.8-3.0 (m, 2H), 2.5-2.6 (m, 4H), 1.8-2.0 (m, 2H), 1.5-1.8, 1.0-1.2 (m, 6H), 1.2-1.4 (m, 14H). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$): δ (ppm) 170.6, 170.4, 168.9, 167.6, 120.4, 114.6, 62.3, 62.1, 61.9, 61.7, 59.3, 51.5, 49.3, 38.8, 36.2, 34.2, 33.8, 31.7, 30.8, 29.9, 28.8, 25.9, 25.8, 25.1, 14.2, 14.1, 14.0 ppm. nOe correlation between the vinylic protons on C-10 with a) protons on the cyclohexyl ring, and b) protons on C-6. HRMS calculated for $C_{27}H_{33}NO_9Na$ (M^+Na) 538.2053, found 538.2061.



11

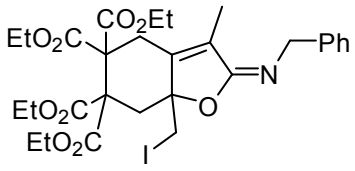
Preparation of tetraethyl-3-oxo-2-phenyl-3,4,4a,5-tetrahydroisoquinoline-6,6,7,7(2H,8H)-tetracarboxylate (11): General procedure **1** was used with enyne **1f** (100 mg, 0.25 mmol), phenyl isocyanate (30.14 mg, 0.25 mmol), $NiCOD_2$ (6.87 mg, 0.025 mmol), IPr (19.41 mg, 0.050 mmol) and toluene 2.5 ml were stirred

for 4 hours at 80 °C. The crude compound was purified by flash chromatography eluting with 30% EtOAc/hexanes to yield compound **11** as an oil (25.4 mg, 19%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.39 (t, *J*= 2H), 7.23-7.29 (m, 3H), 6.09 (s, 1H), 4.17-4.32 (m, 8H), 2.76-2.93 (m, 4H), 2.61-2.50 (m, 2H), 2.26-2.30 (m, 1H), 1.185-1.382 (m, 12H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ (ppm) 171.6, 169.7, 144.2, 138.4, 136.8, 129.5, 129.2, 124.4, 119.9, 114.3, 62.1, 57.5, 41.748, 40.572, 17.838, 14.216. nOe correlation between the vinylic proton on C-10 and a) phenyl protons and b) protons on C-6. HMBC correlation between the vinylic proton on C-10 and a) C-8, b) 6, and c) C-1'. **HRMS** *m/z* calculated for $C_{28}H_{41}NO_9Na$ (M^+Na) 544.2523, found 544.2514



12

(E)-tetraethyl 2-(benzylimino)-7a-(bromomethyl)-3-methyl-7,7a-dihydrobenzofuran-5,5,6,6(2H,4H)-tetracarboxylate (**12**) Compound **12** were prepared as described by Wang and co-workers[5]. Under nitrogen atmosphere dienamide ***Z*-3b** (83 mgms, 0.15 mmol) , *N*-bromosuccinimide (27.17 mgms, 0.15 mmol) and 1.5 ml tetrahydrofuran were stirred at room temperature for 3 hours. The reaction mixture was quenched with deionozed water and extracted twice with dichloromethane (10 ml x 2 times). After drying the organic layer with $MgSO_4$, the crude product was isolated and purified by flash chromatography (30% ethyl acetate/ hexanes) to obtain compound **12** (50 mg, 53%) as an oil. ^{1}H NMR (400 MHz, C_6D_6) δ (ppm). 7.58-7.59 (brs, 2H), 7.21 (t, *J*= 8.0, 2H), 7.11 (d, J= 7.2 Hz, 1H), 4.82 (dd, J= 24.4, 15.0 Hz, 2H), 3.80-4.11 (m, 8H), 3.1-3.6 (brm, 6H), 1.79 (s, 3H), 0.86-1.1 (m, 12H) ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): δ (ppm) 170.3, 169.4, 162.2, 145.9, 142.2, 131.1, 128.9, 128.8, 127.9, 127.0, 85.6, 26.8, 62.6, 62.4, 61.5, 60.1, 52.0, 39.2, 30.6, 29.9, 29.2, 29.2, 14.1, 9.9. **HRMS** *m/z* calculated for $C_{29}H_{37}NO_9Br$ (M^+H) 622.50, found 622.1652.



13

(***E*)-tetraethyl-2-(benzylimino)-7a-(iodomethyl)-3-methyl-7,7a-dihydrobenzofuran-5,5,6,6(2H,4H)-tetracarboxylate** (**13)**: Compound **13** was prepared as described by Wang and co-workers[5]. Under nitrogen atmosphere compound ***Z*-3b** (30 mgms, 0.06 mmol) and iodine (16.8 mgms, 0.07 mmol) and dichloromethane 0.6 ml were stirred at room temperature for 8 hours. The reaction was quenched with 1 ml deionozed water and extracted with dichloromethane (5 ml x 2). The organic layers were dried over $MgSO_4$. The crude product was isolated and purified using flash chromatography with 30% ethyl acetate/ hexanes to yield compound **13** (33.6 mg, 90%) as an oil. ^{1}H NMR (400 MHz ^{1}H NMR (400 MHz, C_6D_6) δ (ppm) 7.58-7.59 (brs, 2H), 7.21 (t, *J*= 8.0, 2H), 7.11 (d, *J*= 7.2 Hz, 1H), 4.82 (dd, *J*= 24.4, 15.0 Hz, 2H), 3.80-4.11 (m, 8H), 3.1-3.6 (brm, 6H), 1.79 (s, 3H), 0.86-1.1 (m, 12H). ^{13}C {^{13}H} NMR (75 MHz, $CDCl_3$): 170.3, 169.4, 162.2,

145.9, 142.2, 131.1, 128.9, 128.8, 127.9, 127.0, 85.6, 62.8, 62.6, 62.3, 61.5, 60.1, 52.0, 39.2, 30.6, 30.3, 30.3, 29.9. 29.2, 14.1, 9.9. **HRMS** calculated for $C_{29}H_{37}NO_9I$ (M^+H) 670.14, found 670.1497.

References:

1. Tekavac, T.; Louie, J. *J. Org. Chem*. **2008**, *73*, 2641.

2. (a) Böhm, V. P. W., Gstöttmayr, C. W. K., Weskamp, T.; Herrmann, W. A. *Angew. Chem. Int. Ed.* **2001**, *40,* 3387. (b) Arduengo, A. J. III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J. Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523. (c) Böhm, V. P. W.; Weskammp, T.; Gstottmayr, W. K.; Herrmann, W. A. *Angew. Chem. Int. Ed.* **2000**, *39*, 1602.

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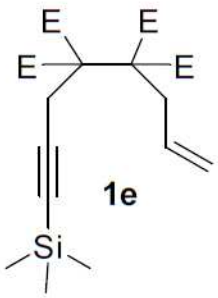
5. Wang, C.; Lu, J.; Mao, G.; Xi, Z. *J. Org. Chem*. **2005**, *70*, 5150.



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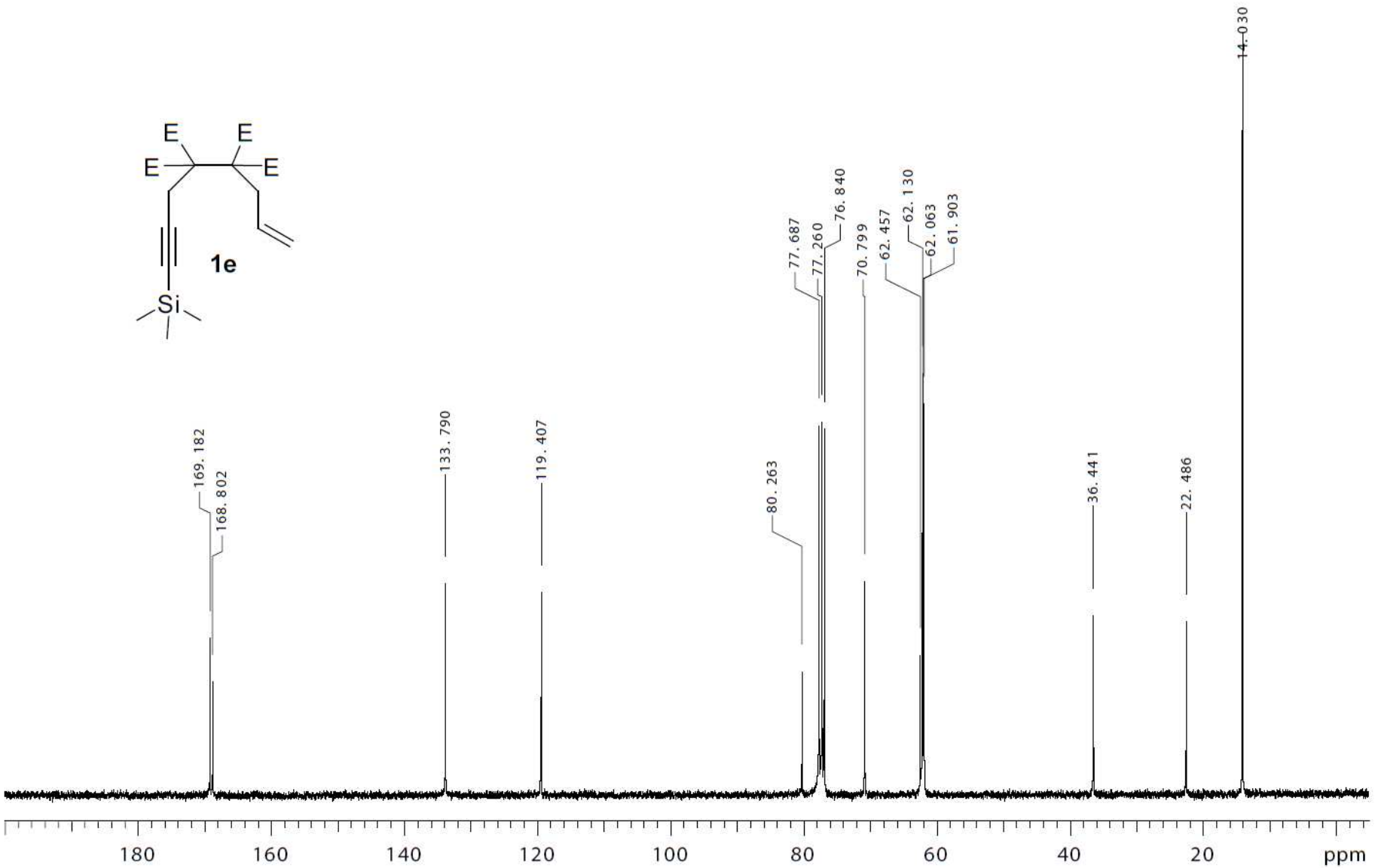
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E
E
1e
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77.260
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62.457
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62.063
61.903
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140
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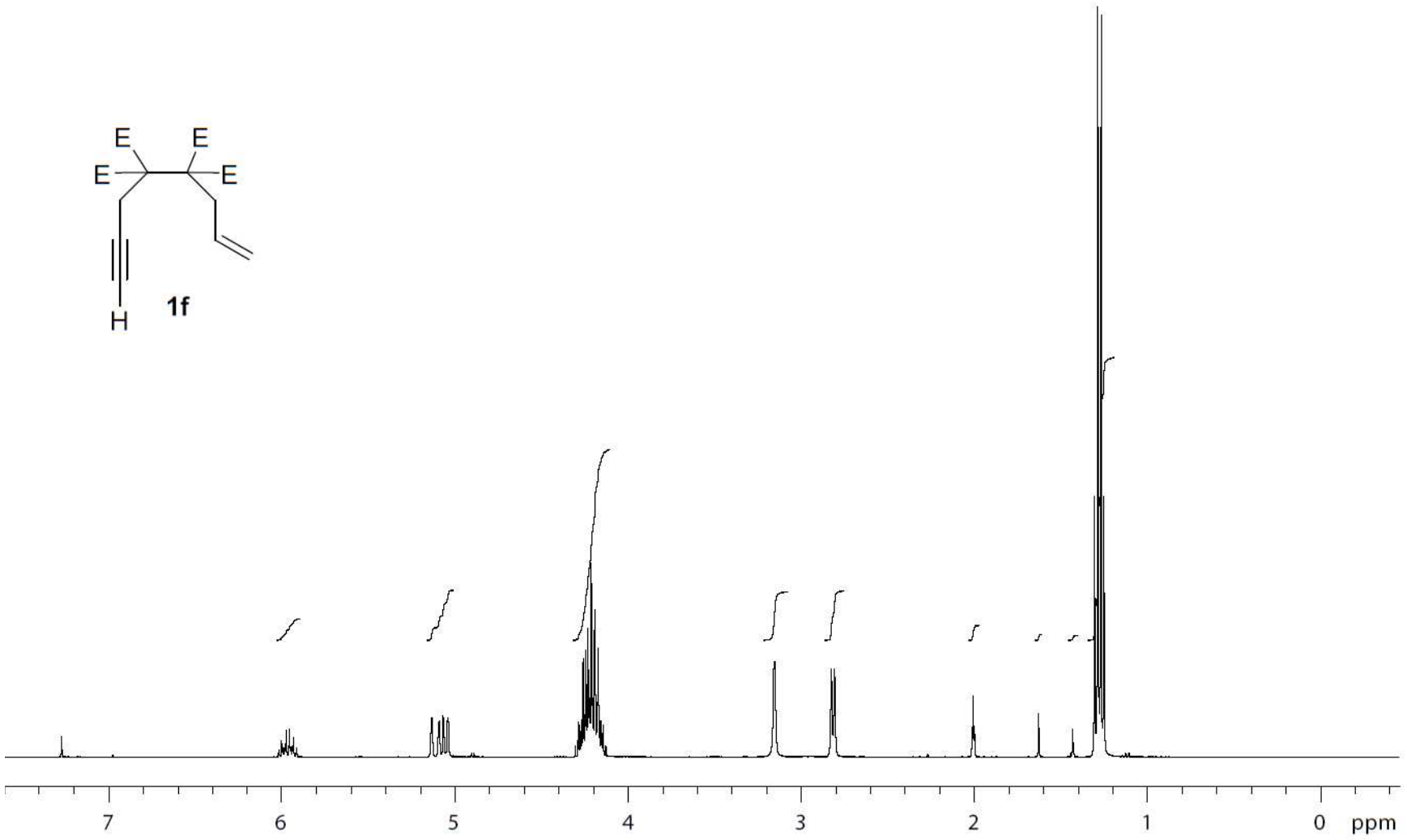
80
60
40
20
ppm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E
E
E
H
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6
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4
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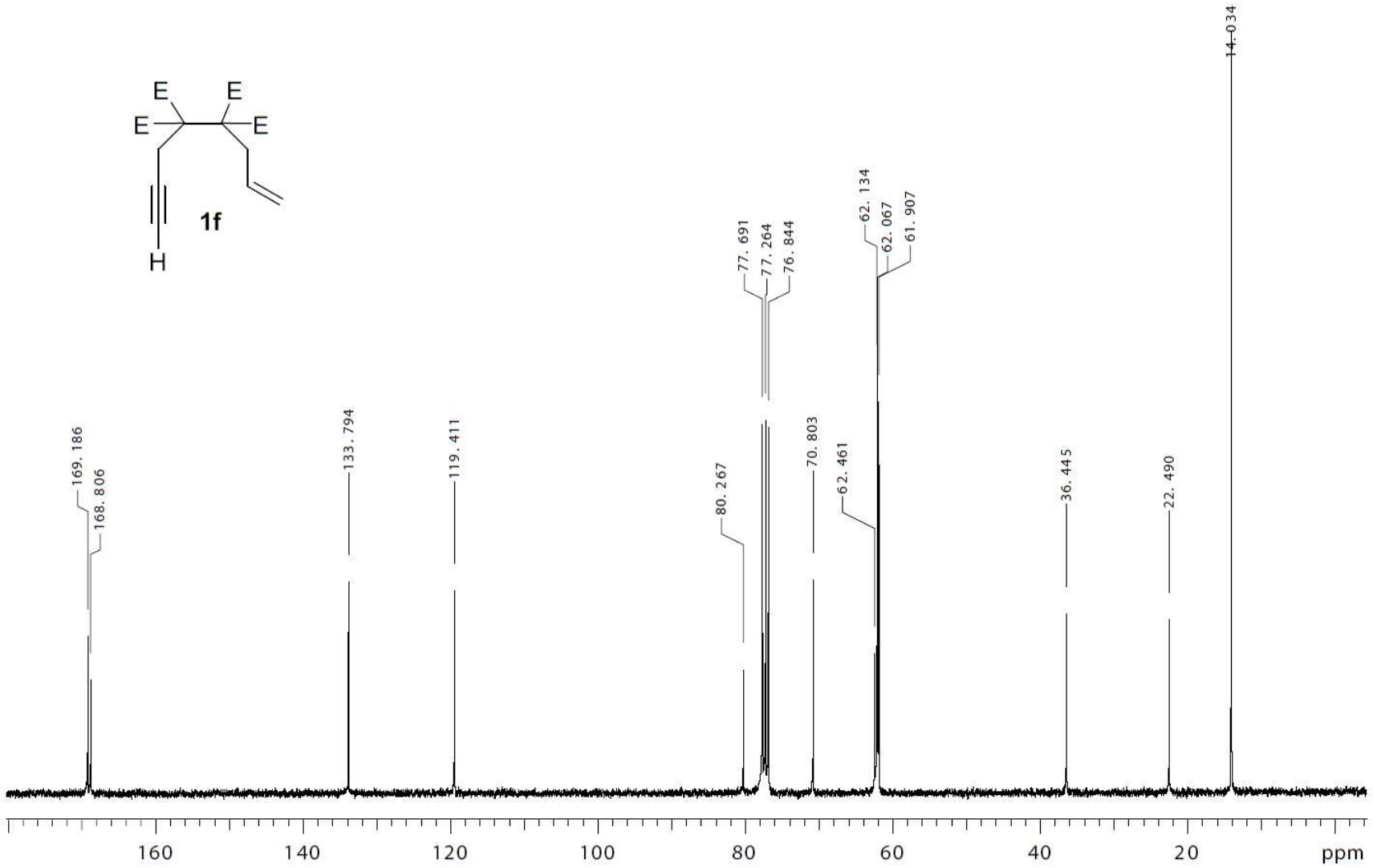
0
ppm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70.803
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61.907
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80
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40
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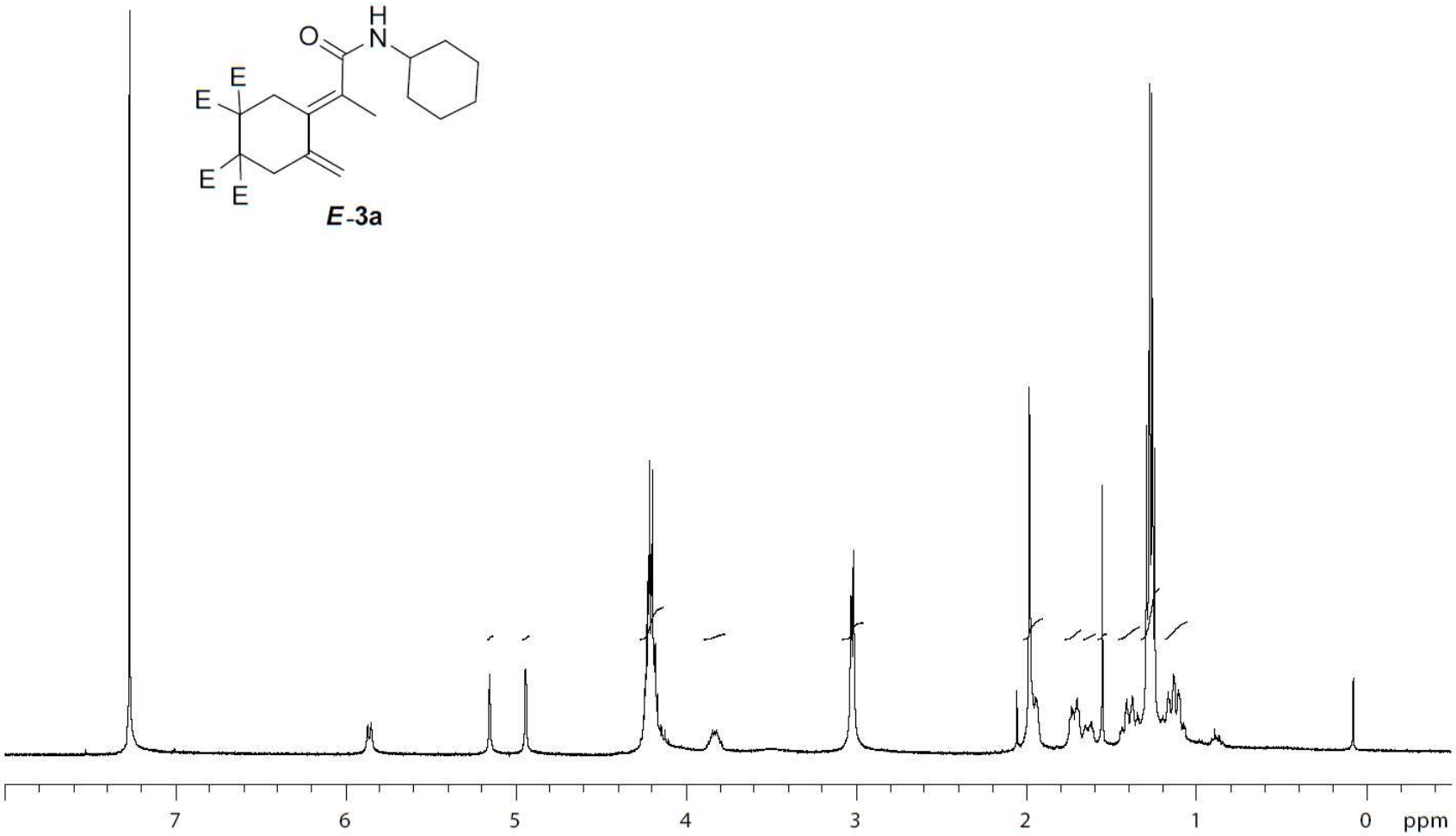
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E
E
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E-3a
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3
2
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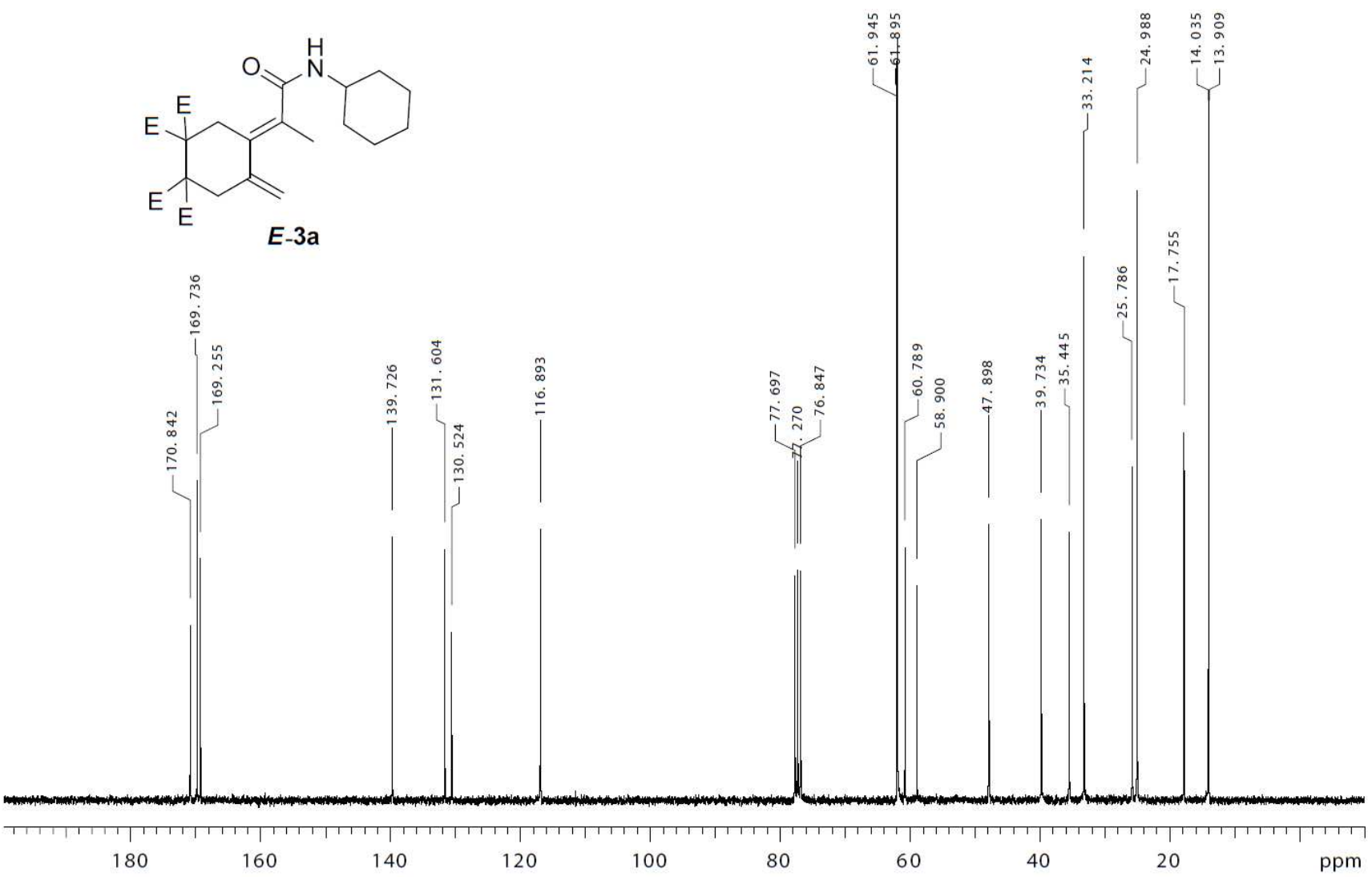
ppm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N
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E
E
E
E
E
E-3a
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116.893
77.697
77.270
76.847
61.945
61.895
60.789
58.900
47.898
39.734
35.445
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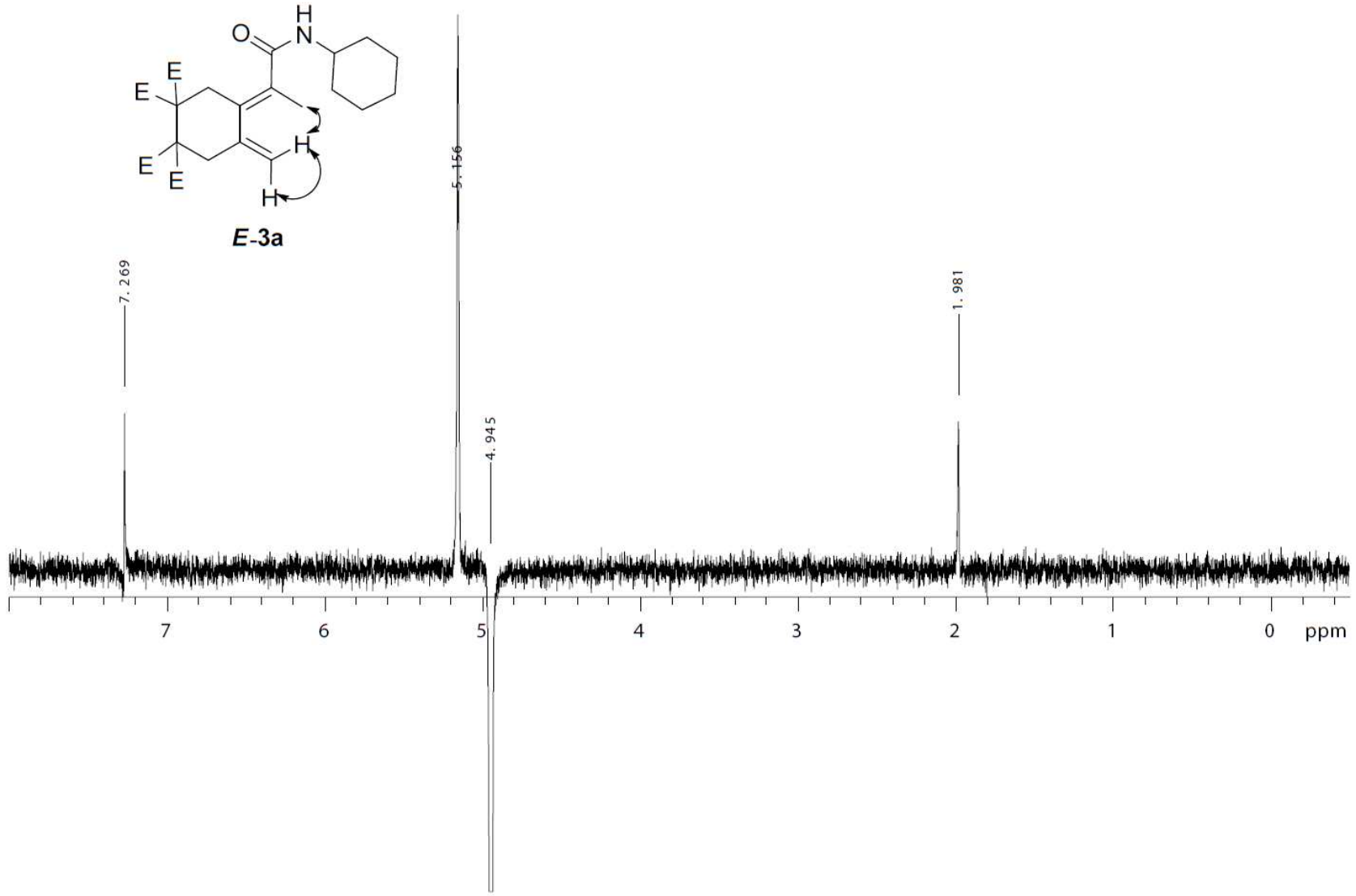
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E
E
H
H
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6
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2
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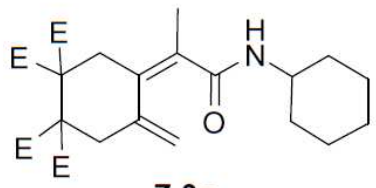
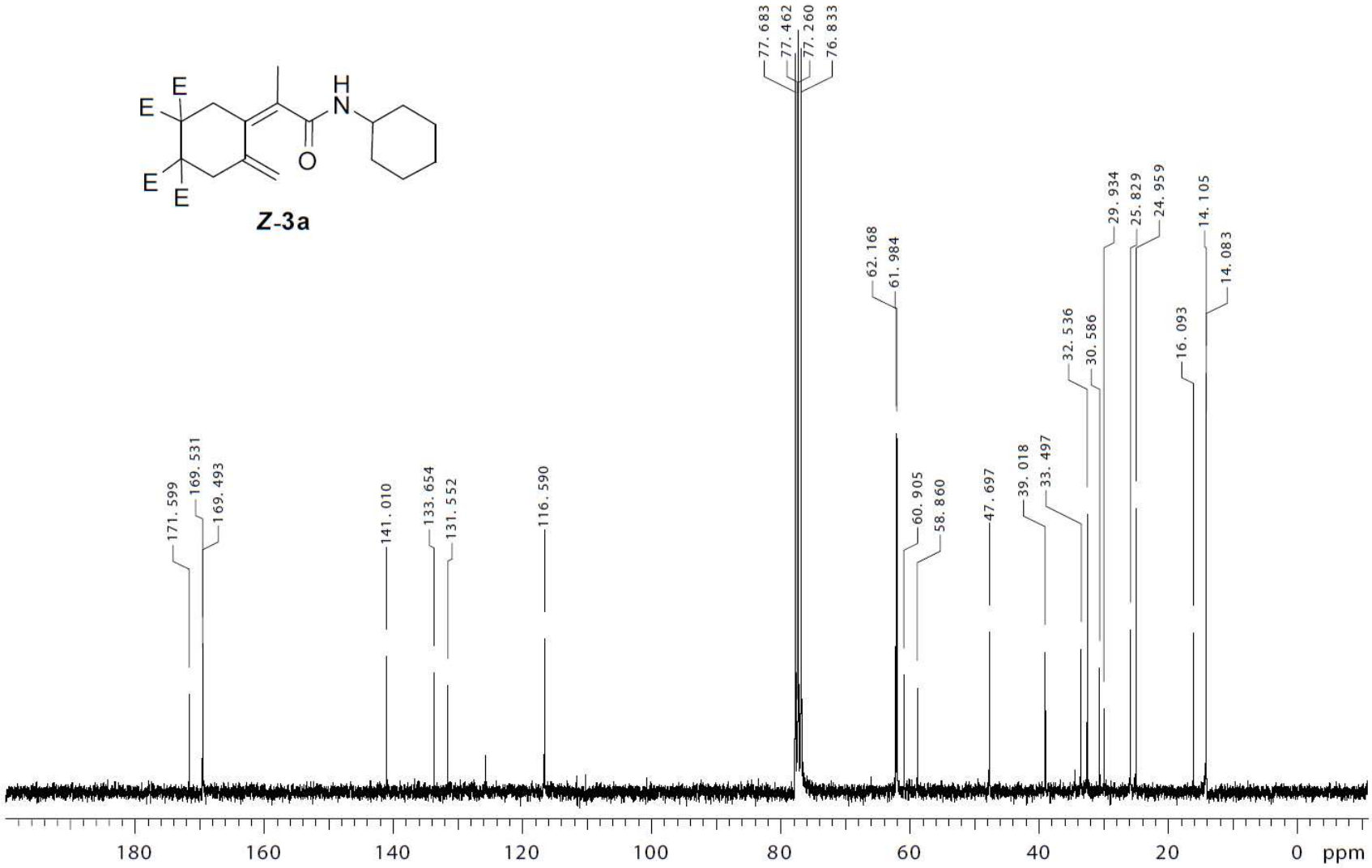


Z-3a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E
E
E
H
N
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62.168
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60.905
58.860
47.697
39.018
33.497
32.536
30.586
29.934
25.829
24.959
16.093
14.105
14.083
171.599
169.531
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133.654
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160
140
120
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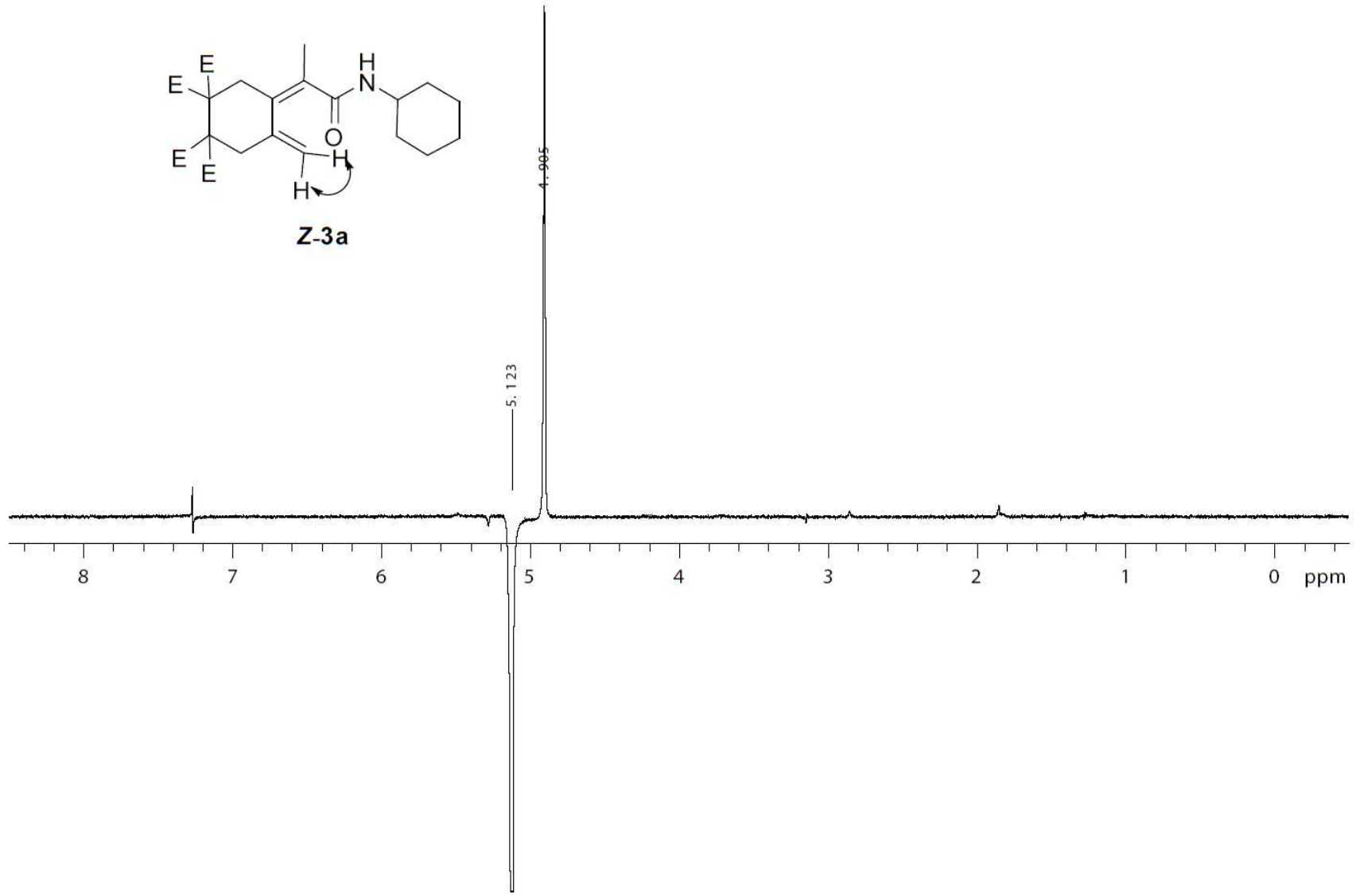
60
40
20
0
ppm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E
E
H
N
O
H
H
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5
4
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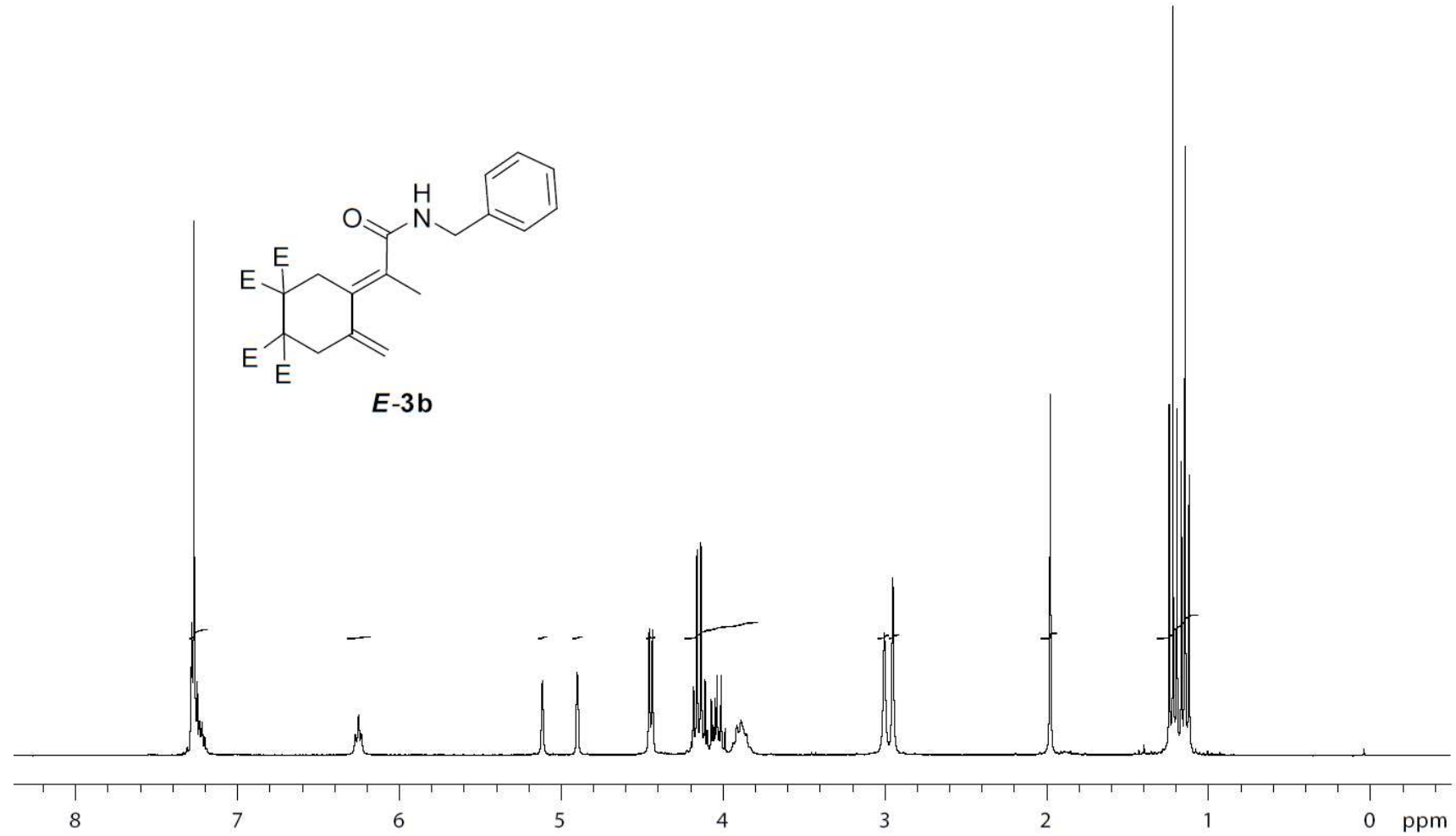
2
1
0
ppm



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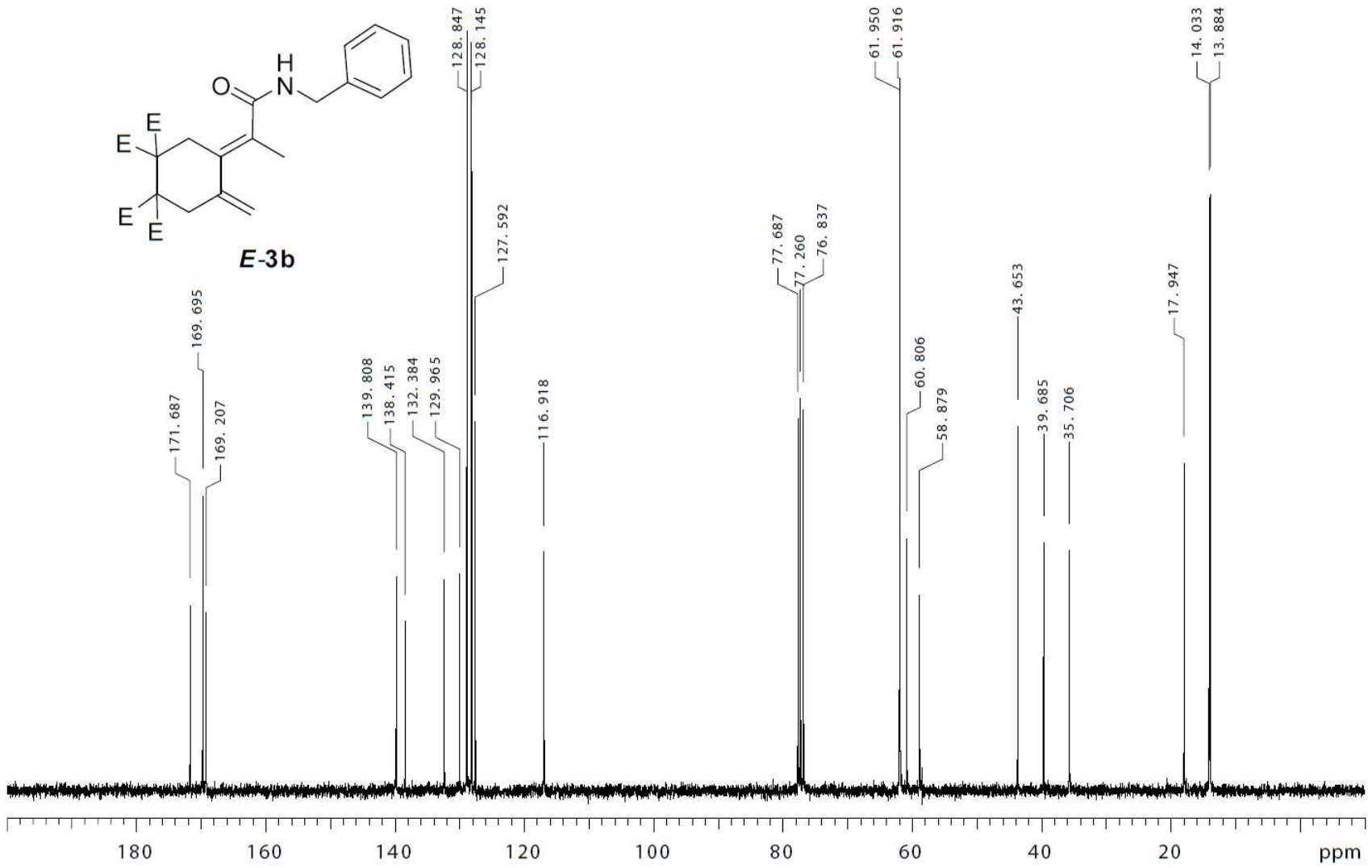
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129.965
128.847
128.145
127.592
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77.687
77.260
76.837
61.950
61.916
60.806
58.879
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140
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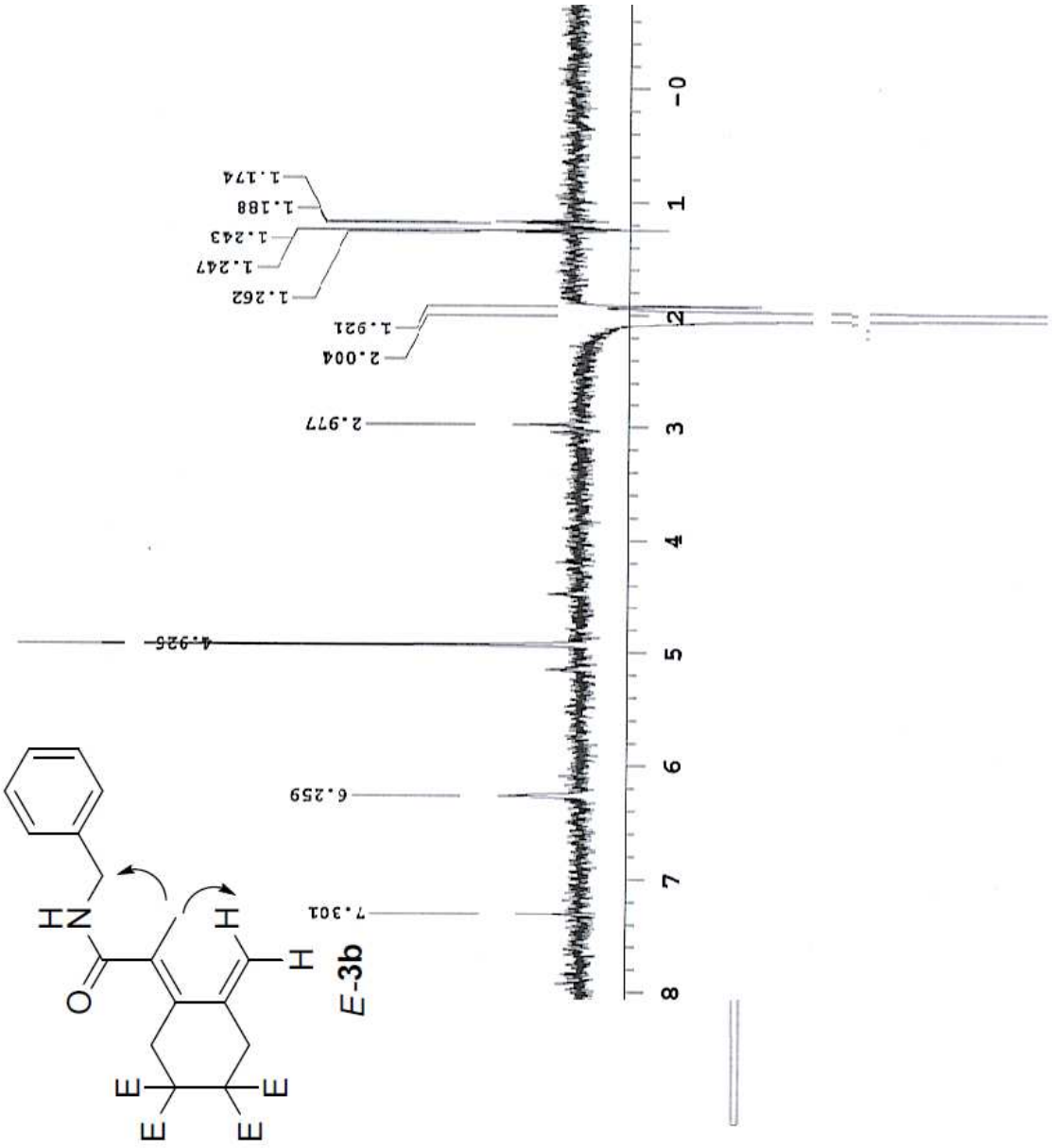
60
40
20
ppm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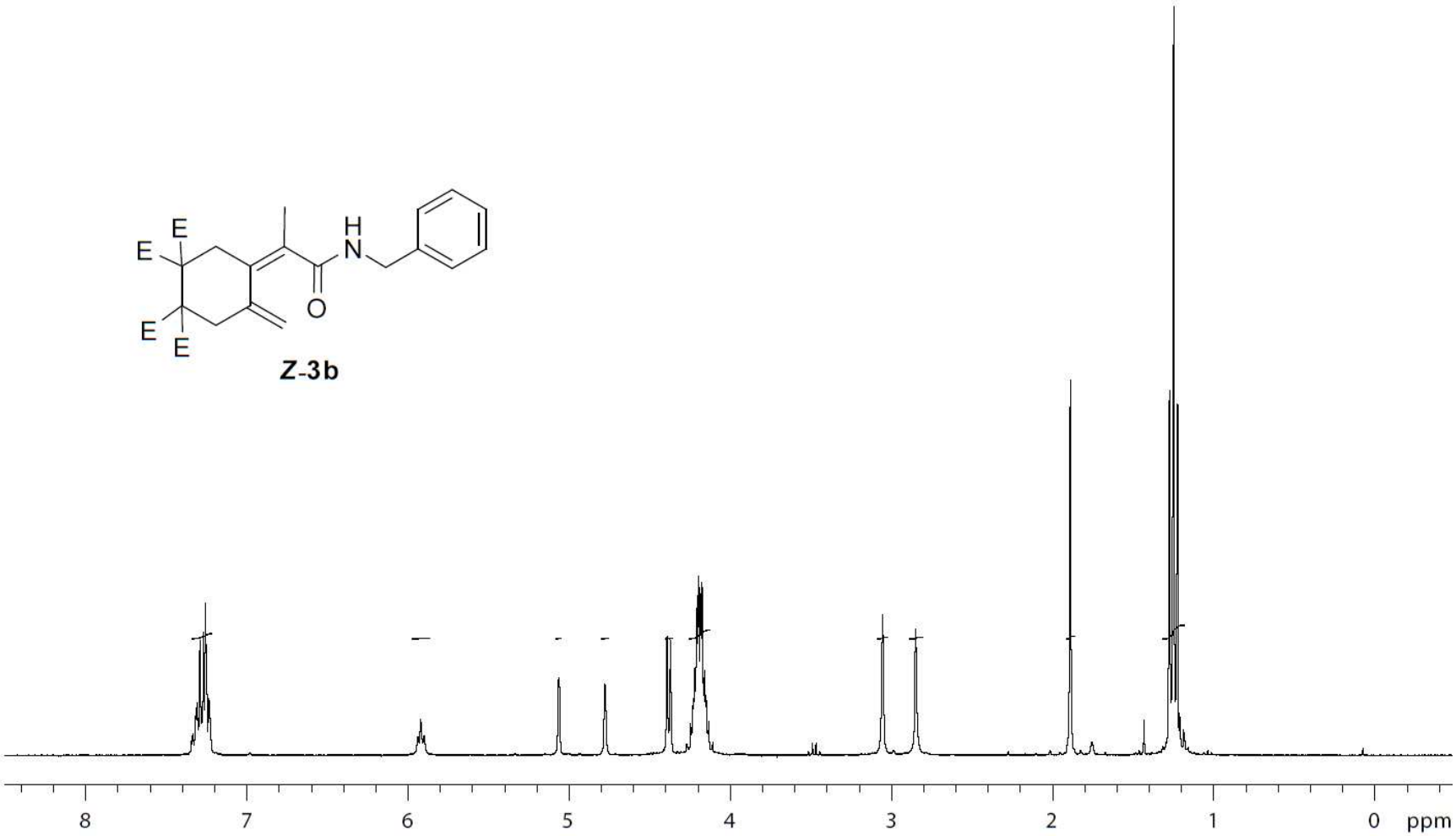
1.247
1.243
1.188
1.174
E-3b



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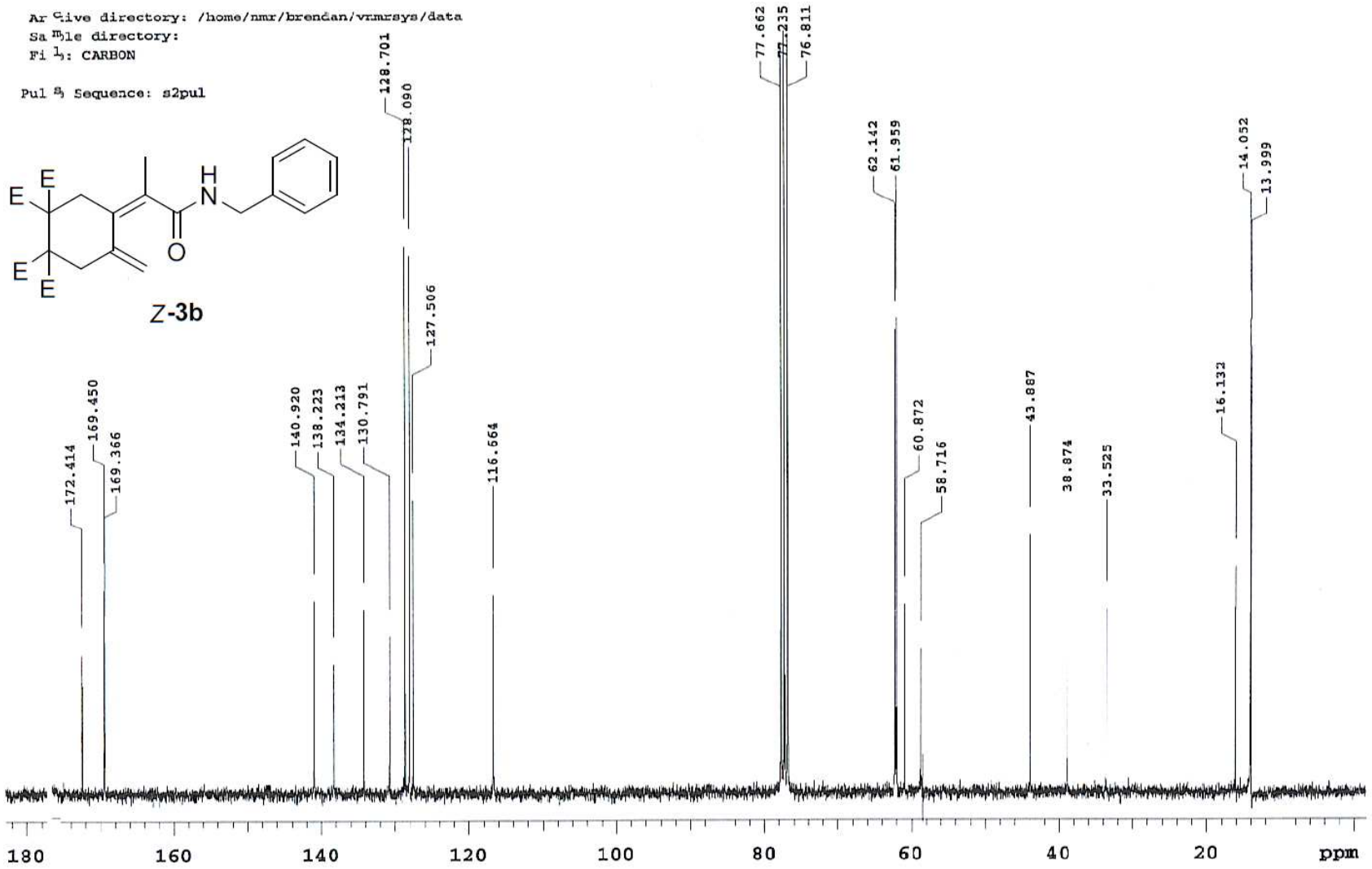
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H
N
O
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134.213
130.791
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128.090
127.506
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77.662
77.235
76.811
62.142
61.959
60.872
58.716
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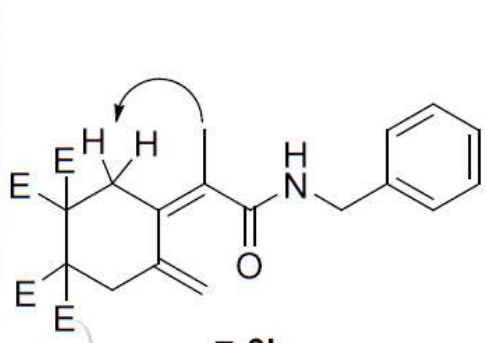
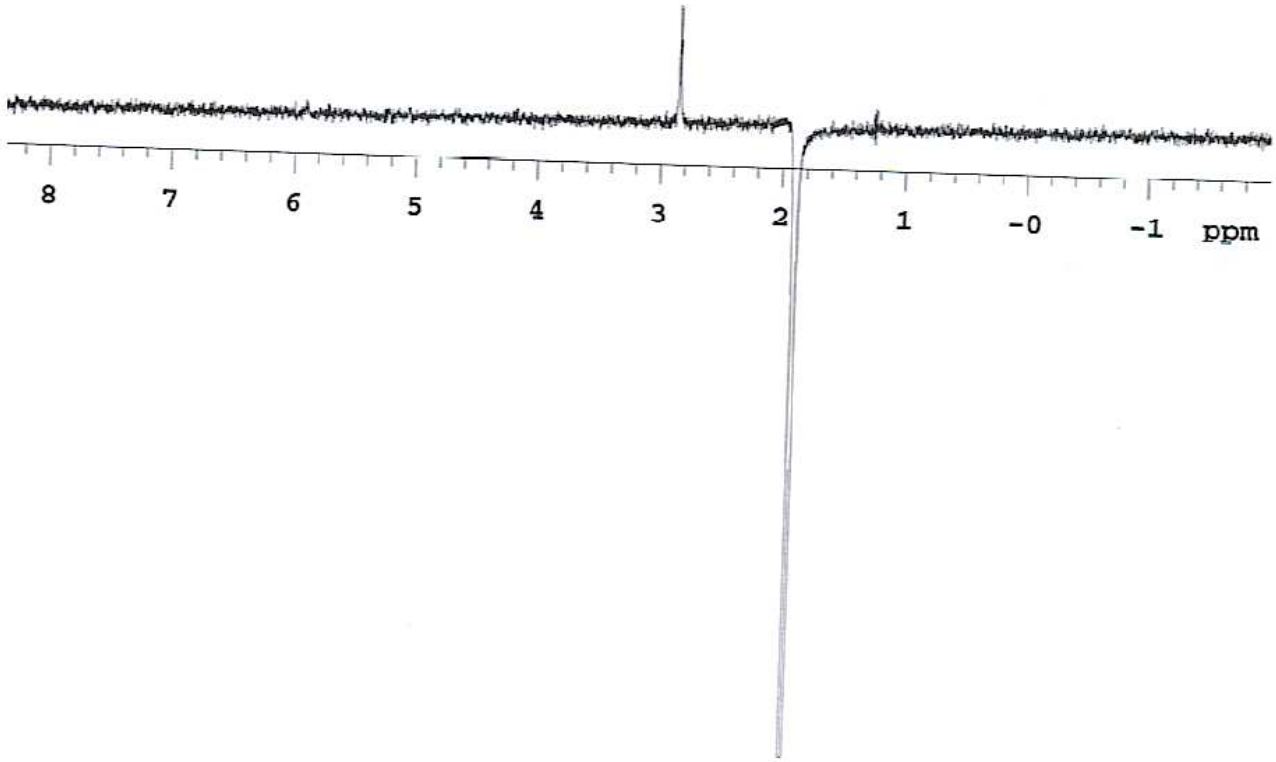
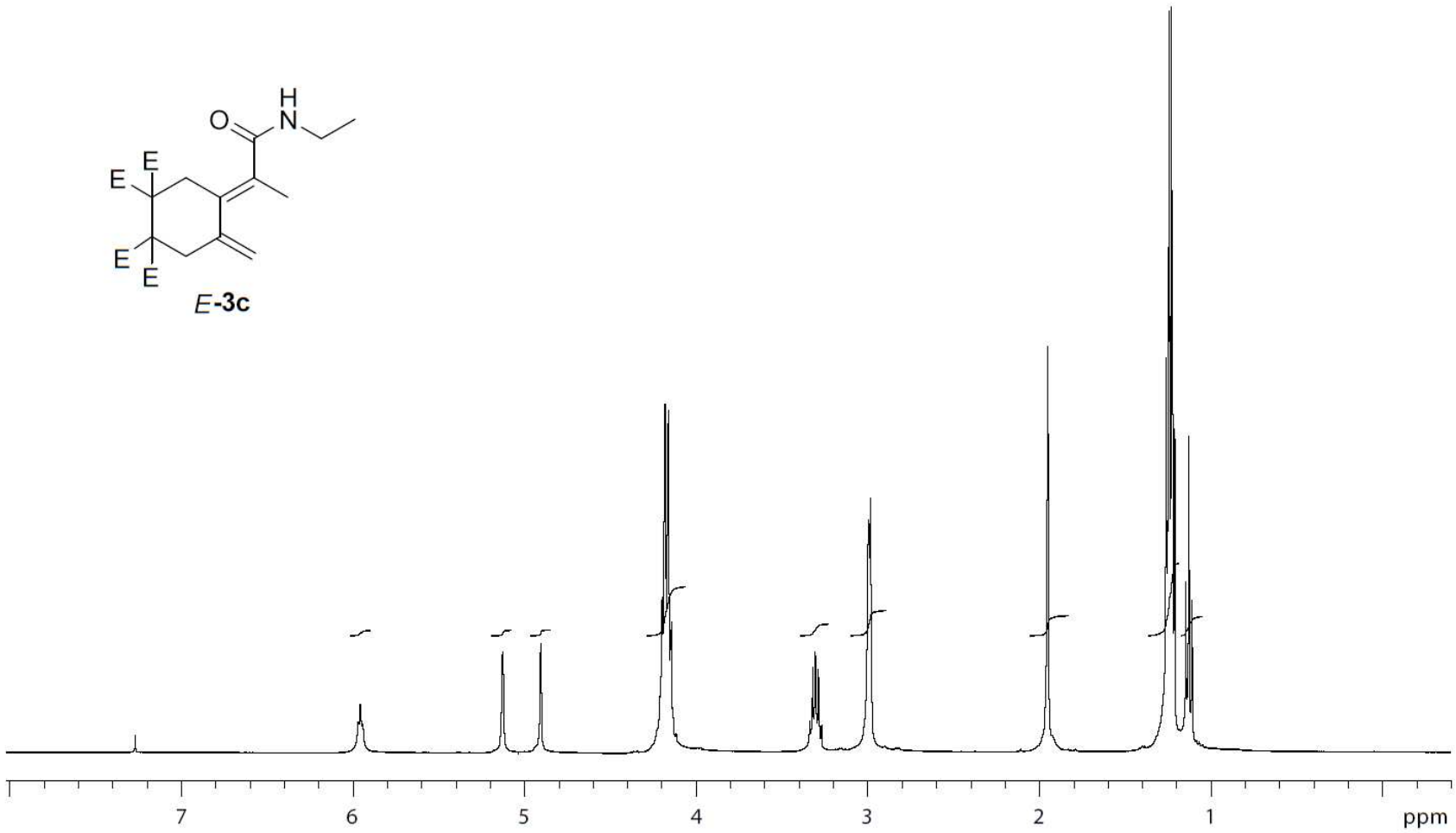
ppm

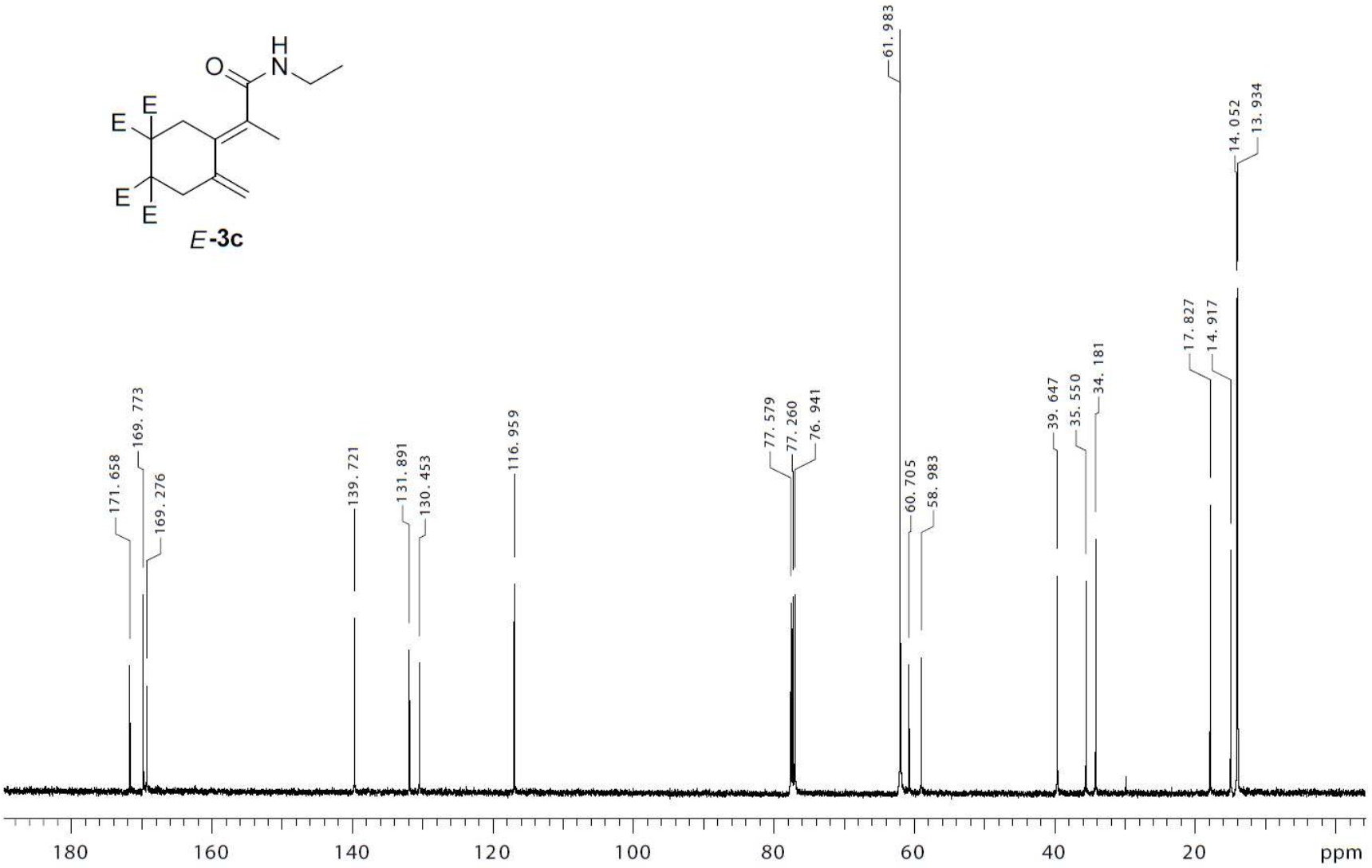


Z-3b





E-**3c**


O
H
N
E
E
E
E
E-3c
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131.891
130.453
116.959
77.579
77.260
76.941
61.983
60.705
58.983
39.647
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14.917
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13.934
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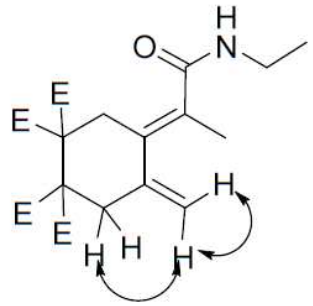
140
120
100
80
60
40
20
ppm



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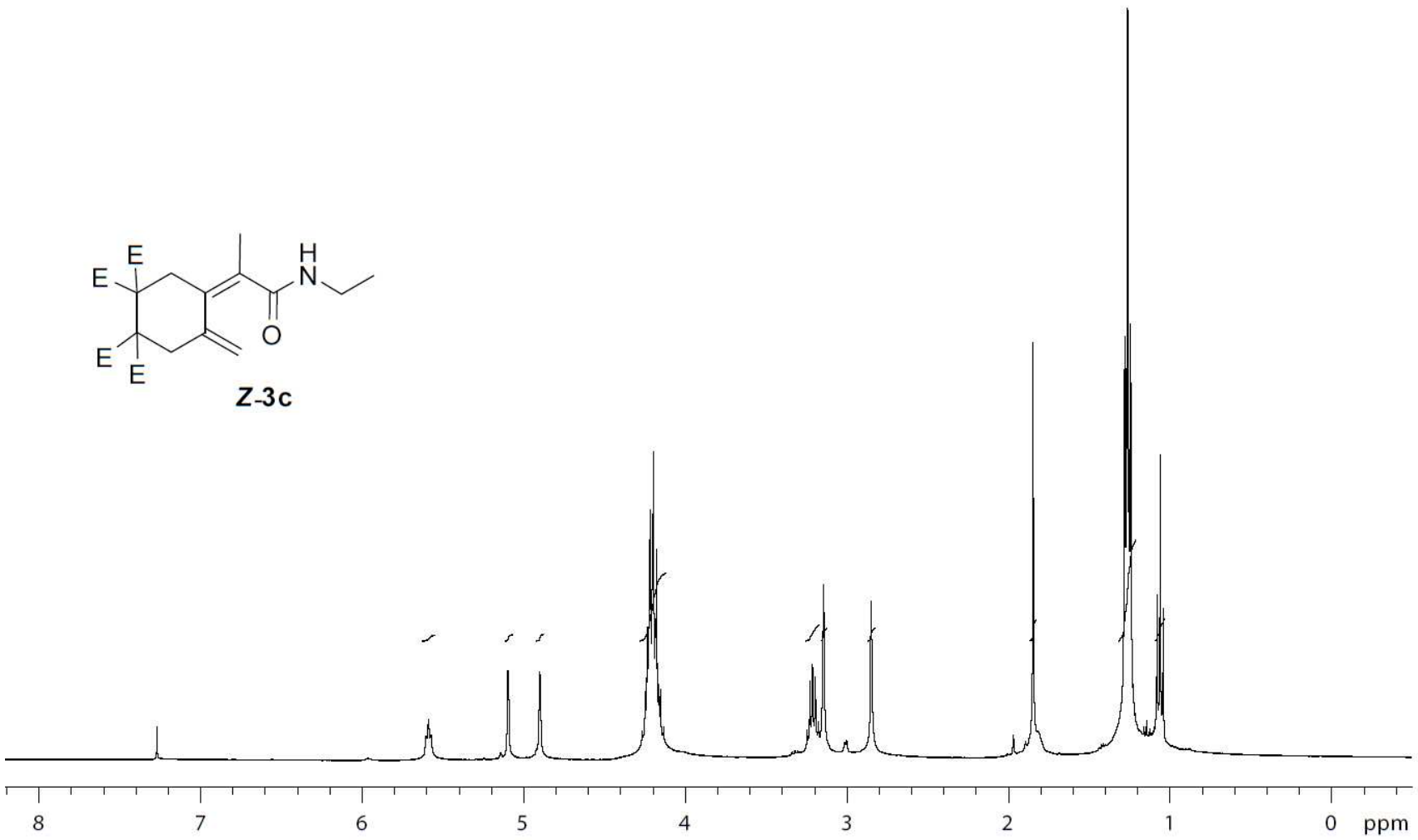

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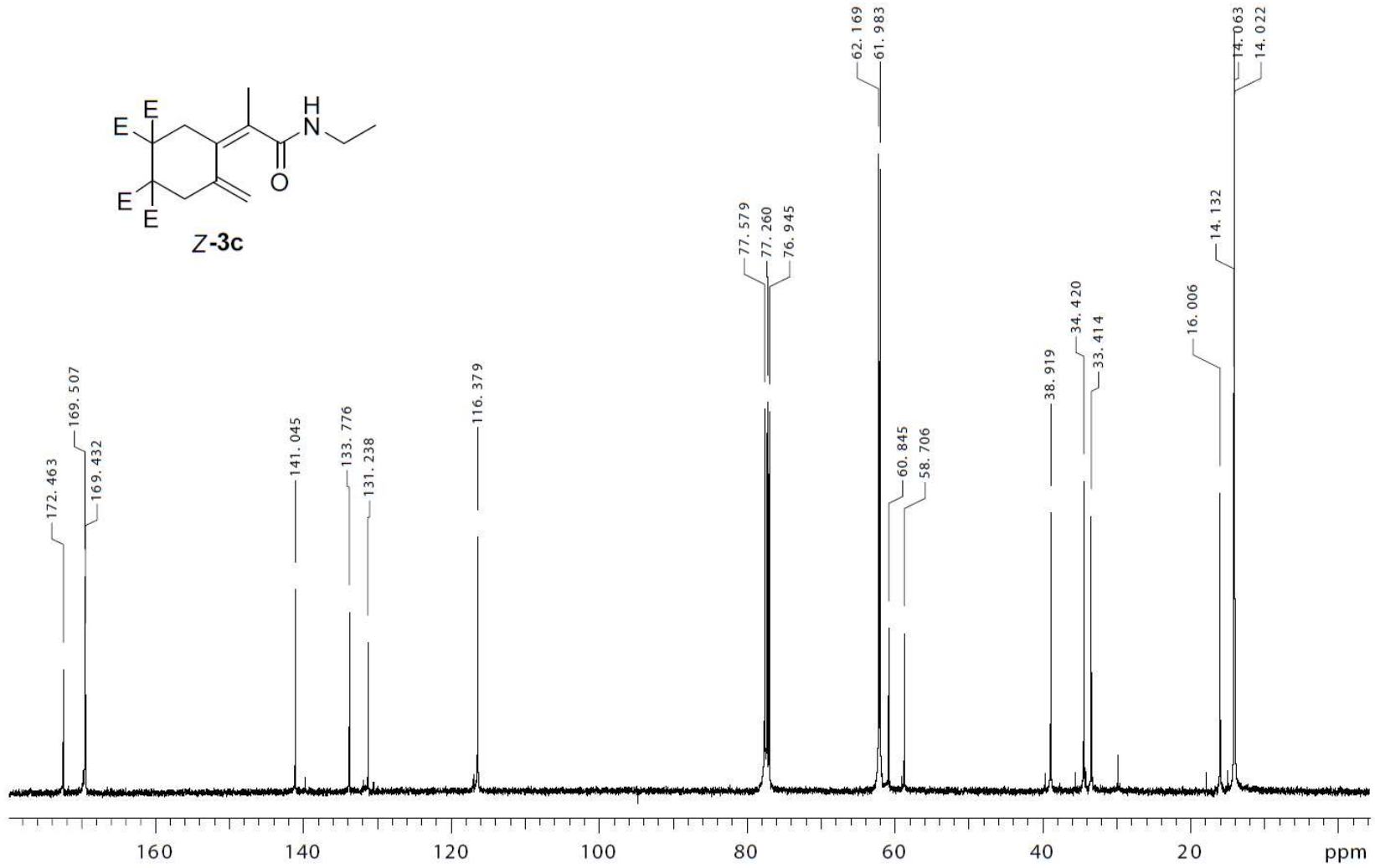
E
E
E
E
H
N
O
Z-3c
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77.579
77.260
76.945
62.169
61.983
60.845
58.706
38.919
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140
120
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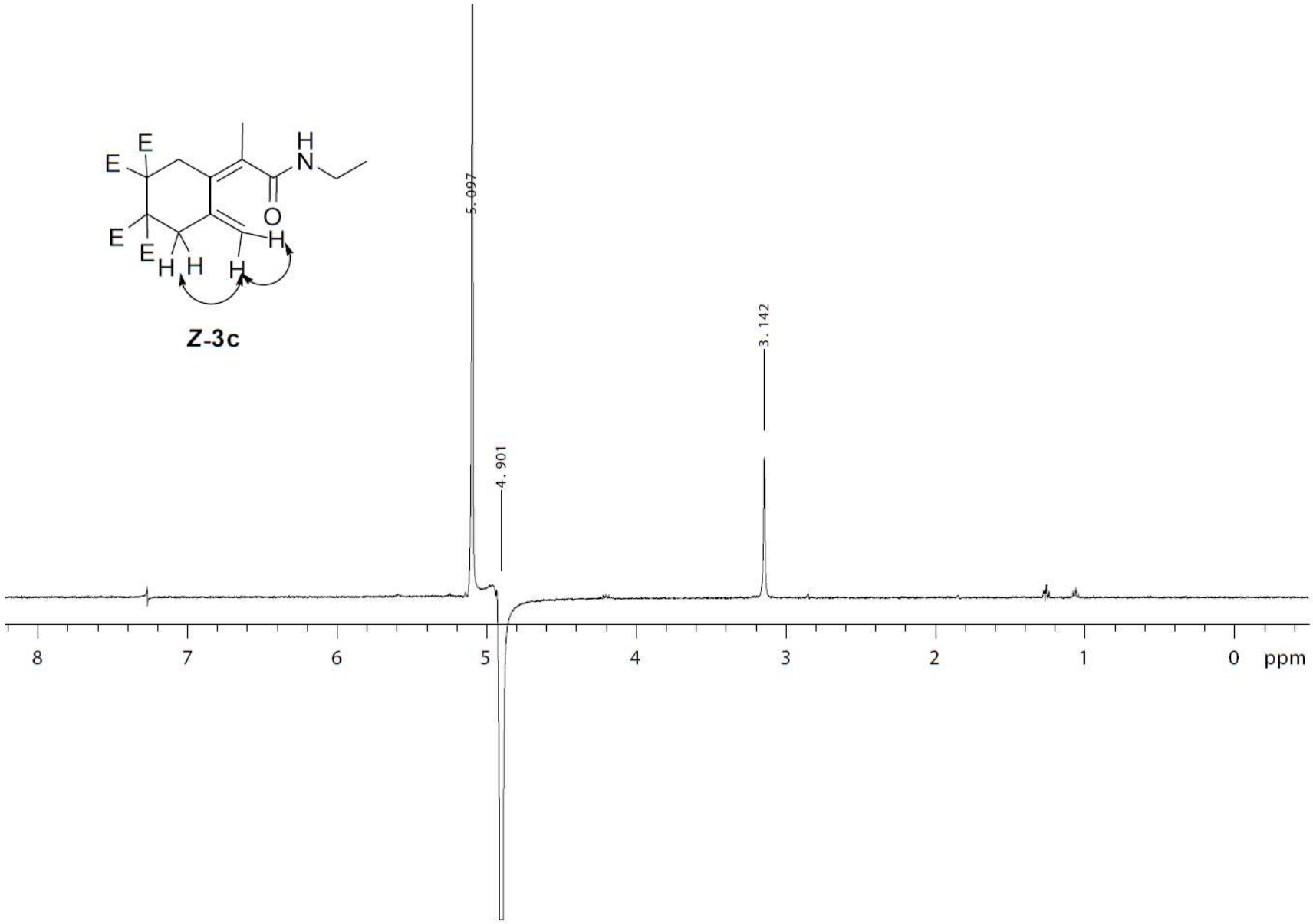
80
60
40
20
ppm


E
E
E
E
H
H
H
H
N
O
Z-3c
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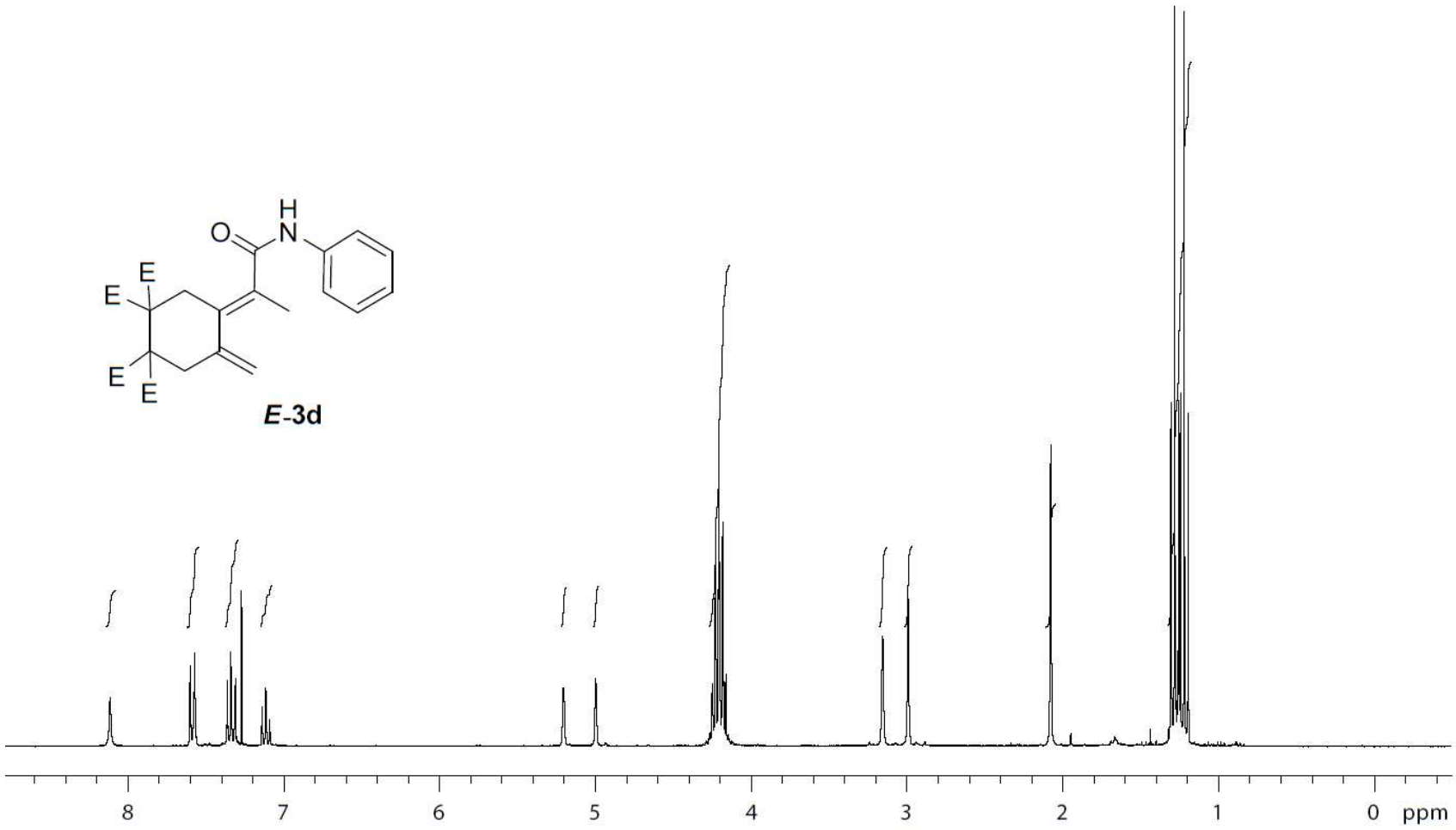
8
7
6
5
4
3
2
1
0
ppm



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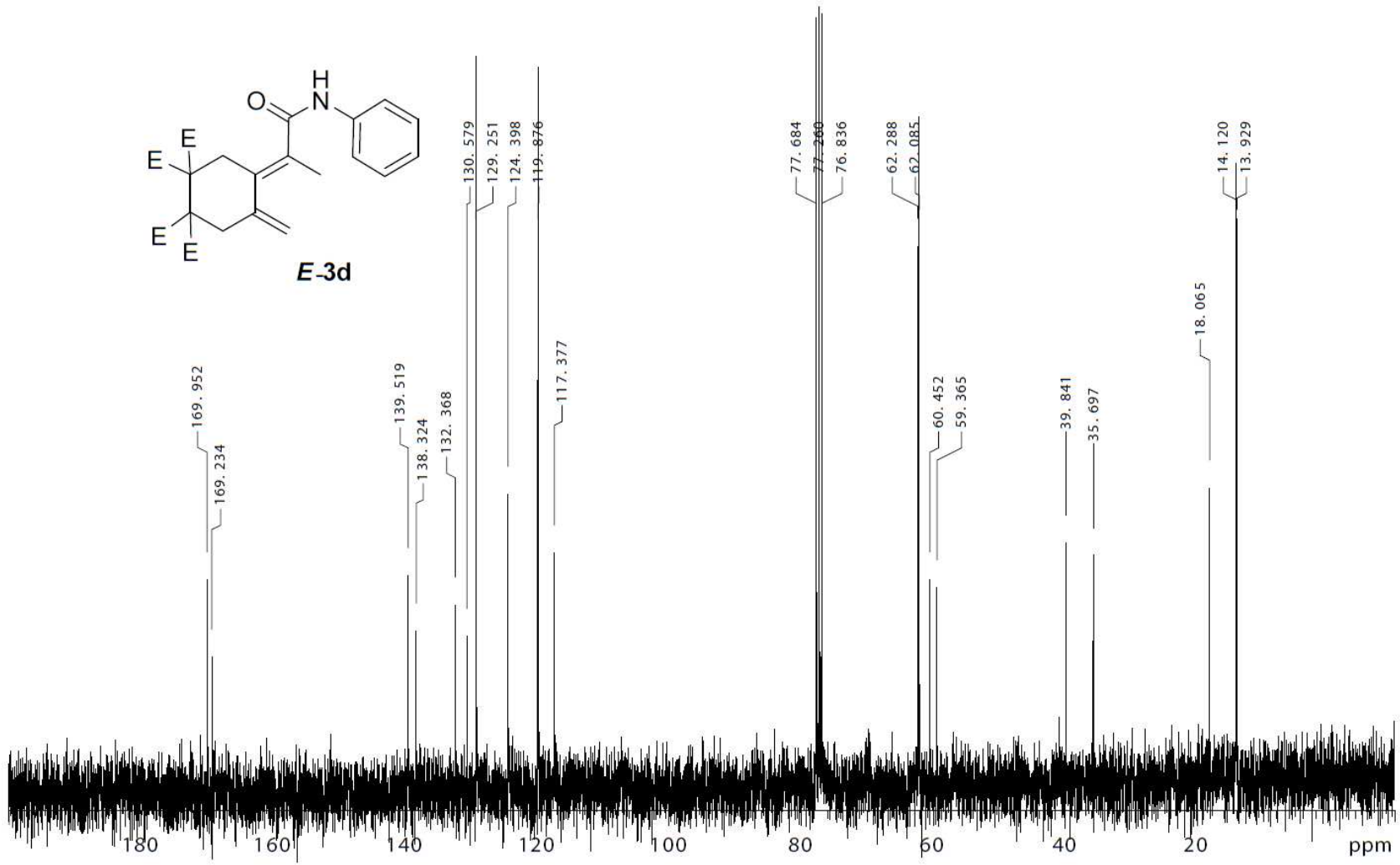
O
H
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E
E
E
E
E
E
E-3d
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139.519
138.324
132.368
130.579
129.251
124.398
119.876
117.377
77.684
77.260
76.836
62.288
62.085
60.452
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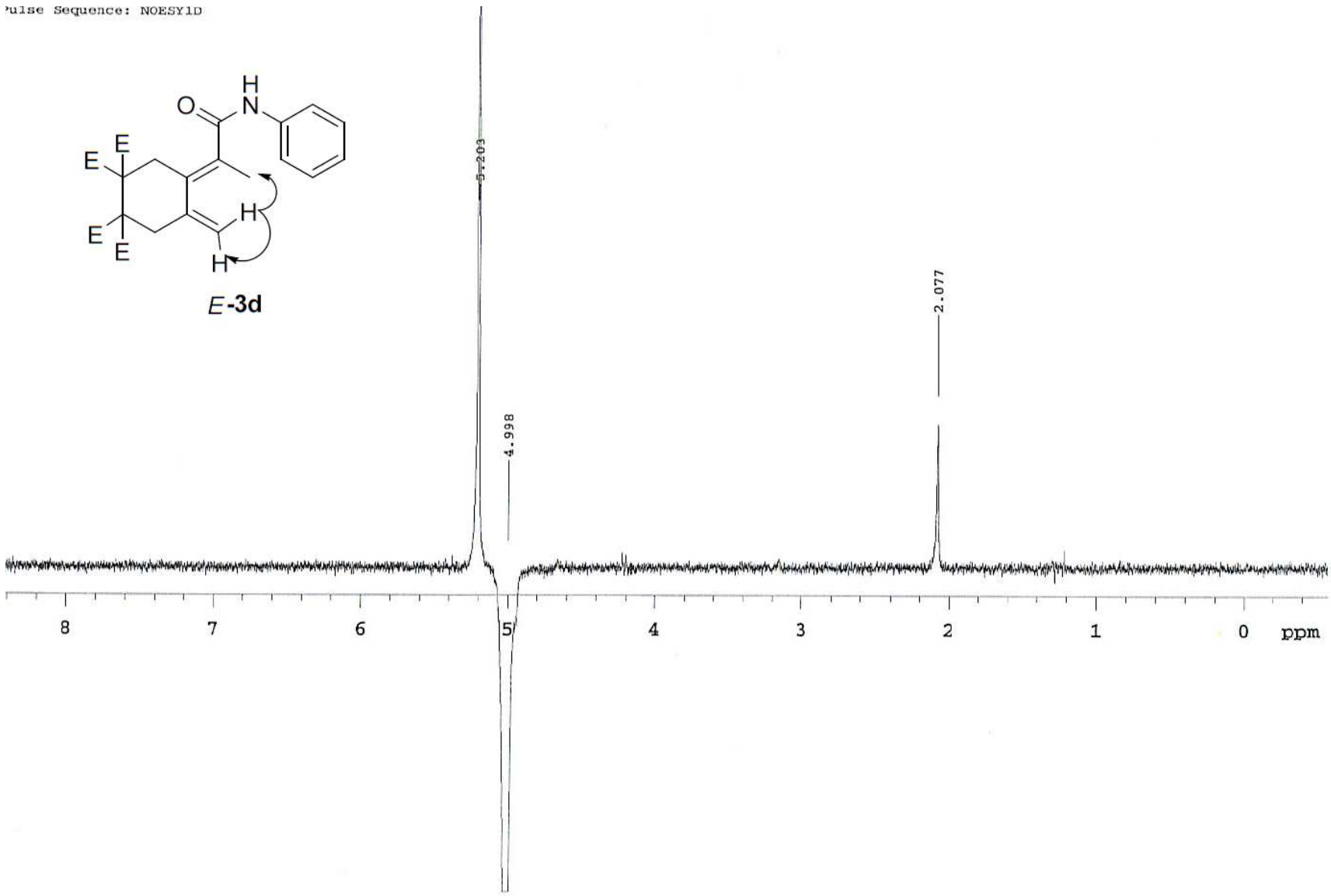
160
140
120
100
80
60
40
20
ppm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H
N
E
E
E
E
H
H
E-3d
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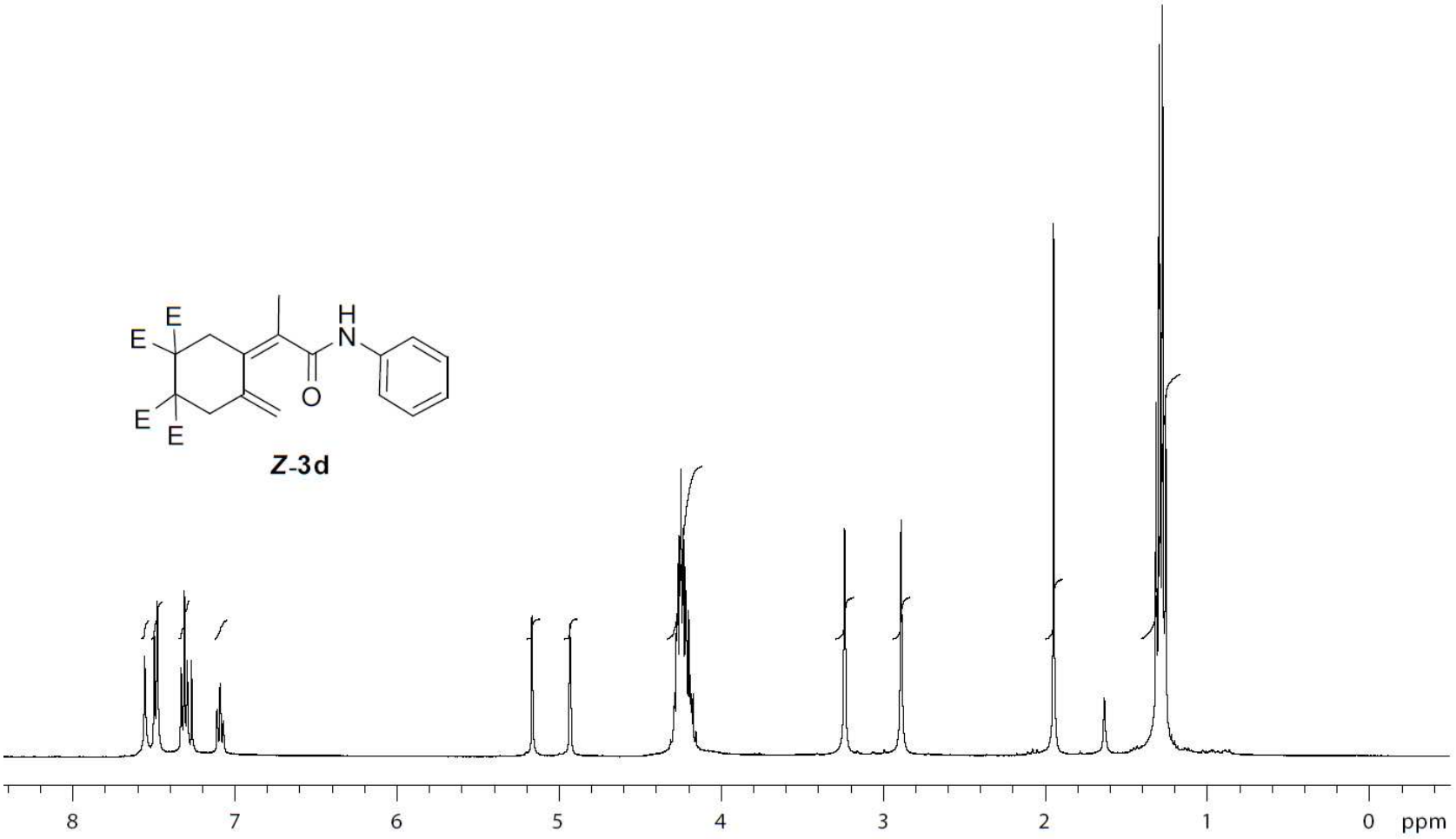
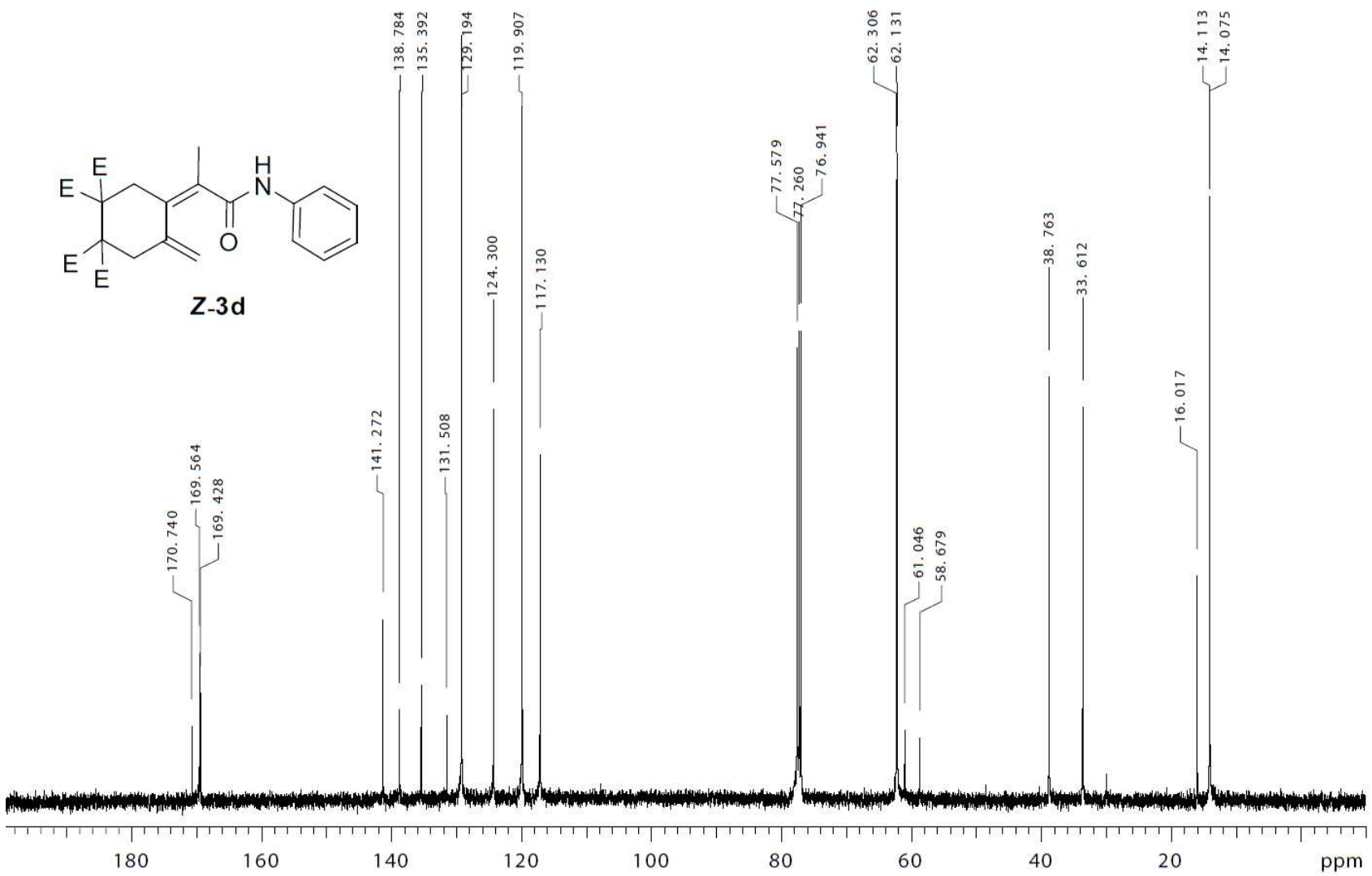
2.077
8
7
6
5
4
3
2
1
0
ppm



***Z*-3d**


E
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E
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H
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O
Z-3d
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135.392
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129.194
124.300
119.907
117.130
77.579
77.260
76.941
62.306
62.131
61.046
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140
120
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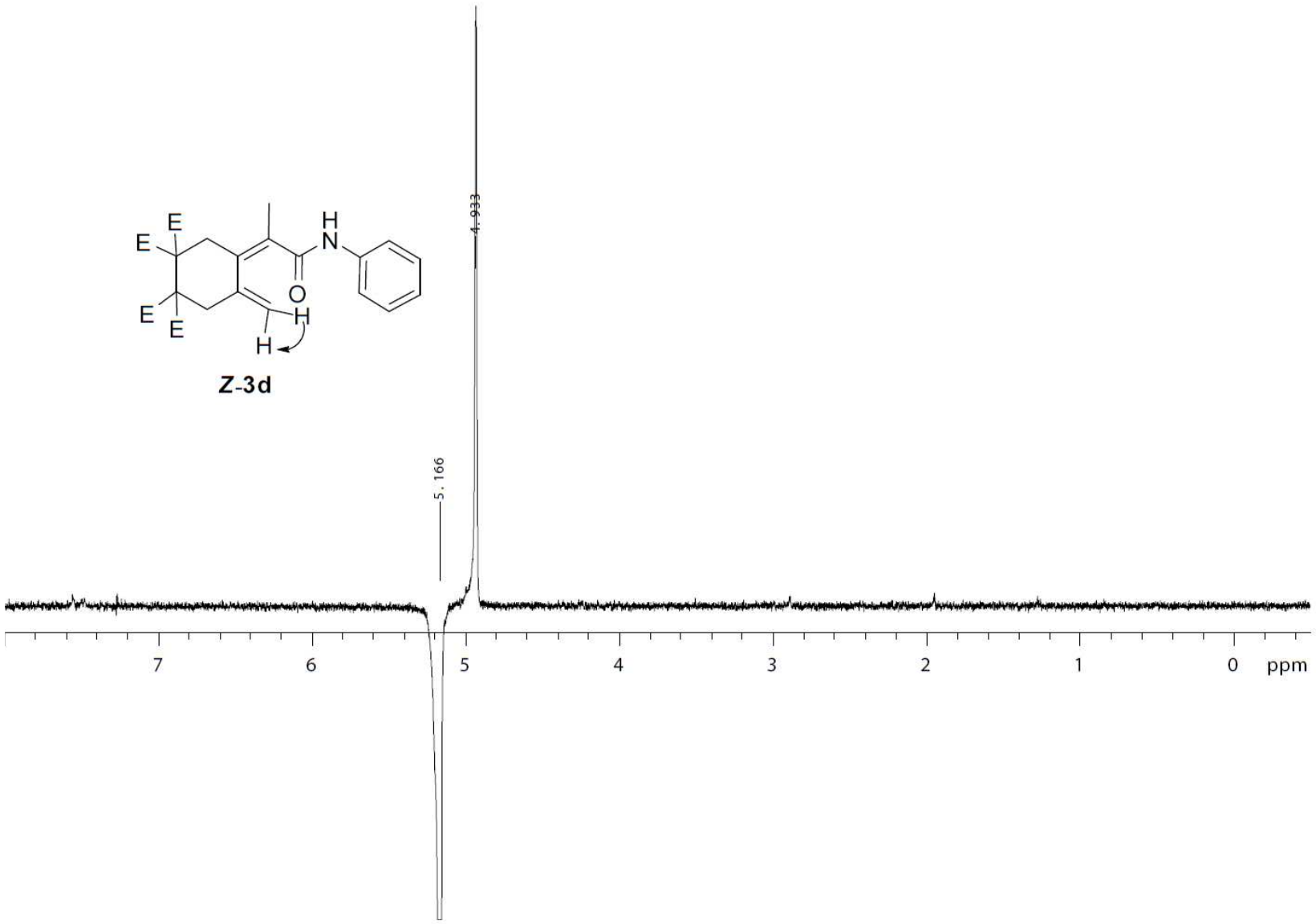
80
60
40
20
ppm


E
E
E
E
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O
H
H
Z-3d
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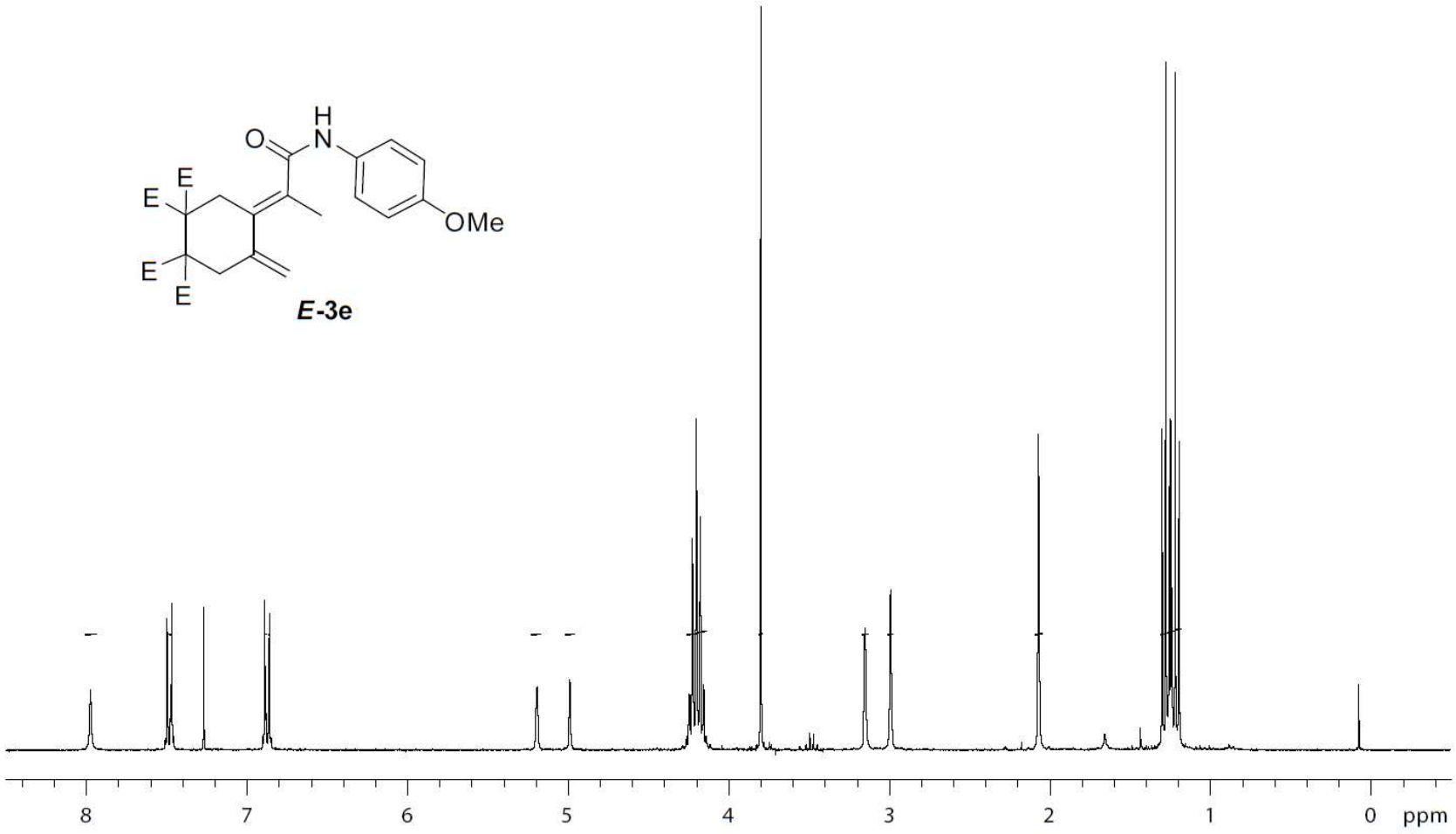
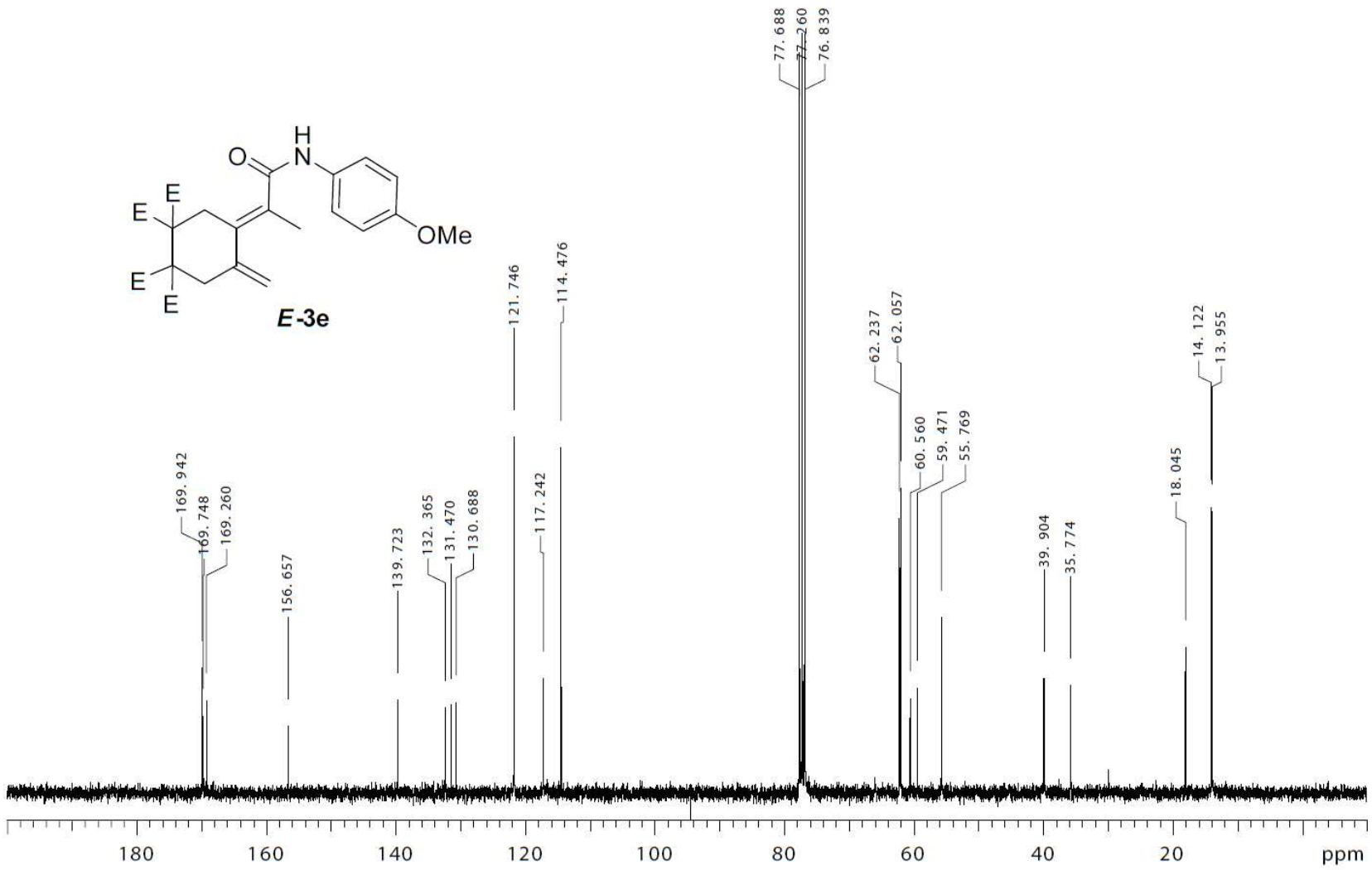
6
5
4
3
2
1
0
ppm



***E*-3e**


O
H
N
E
E
E
E
E
OMe
E-3e
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76.839
121.746
114.476
62.237
62.057
60.560
59.471
55.769
169.942
169.748
169.260
156.657
139.723
132.365
131.470
130.688
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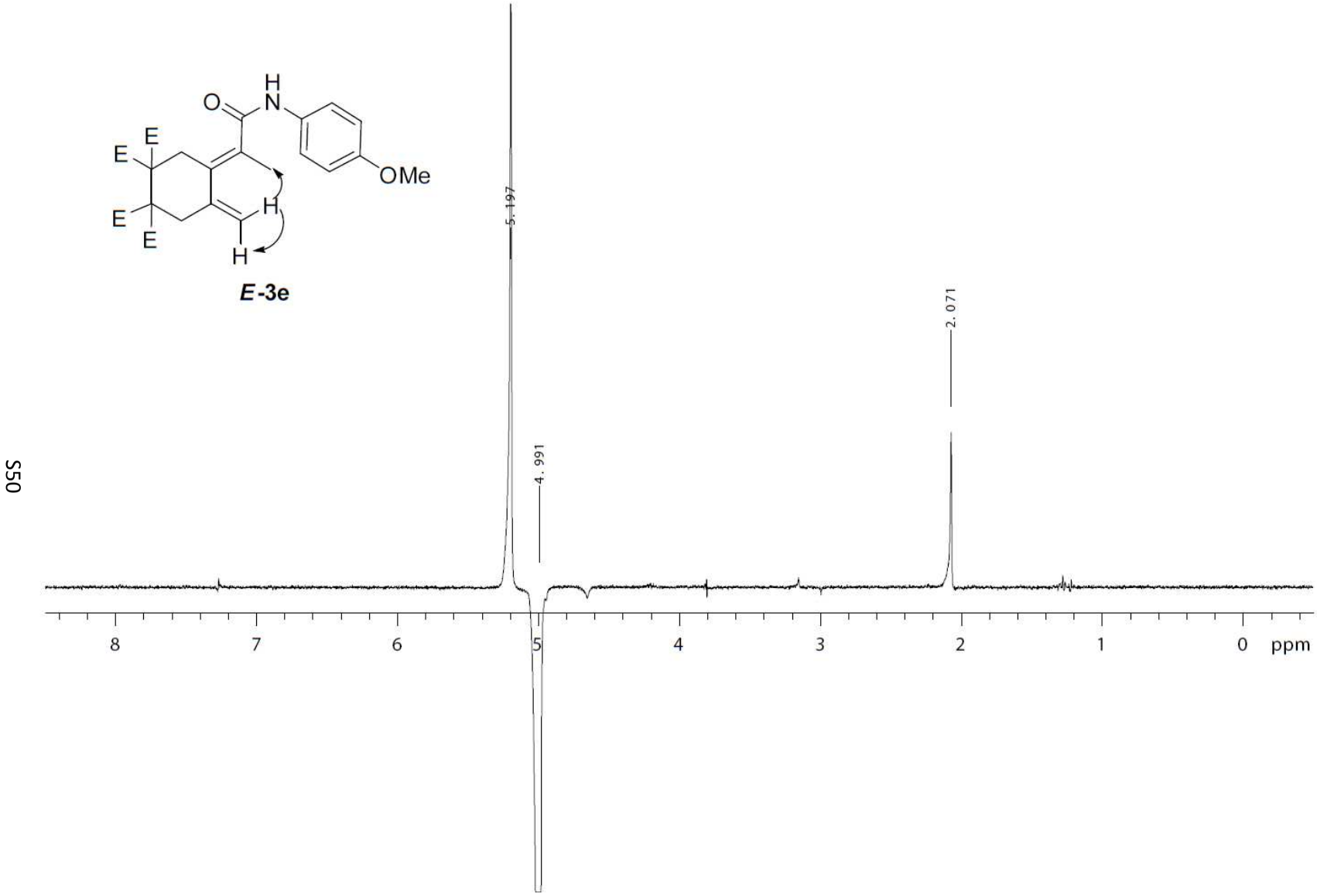
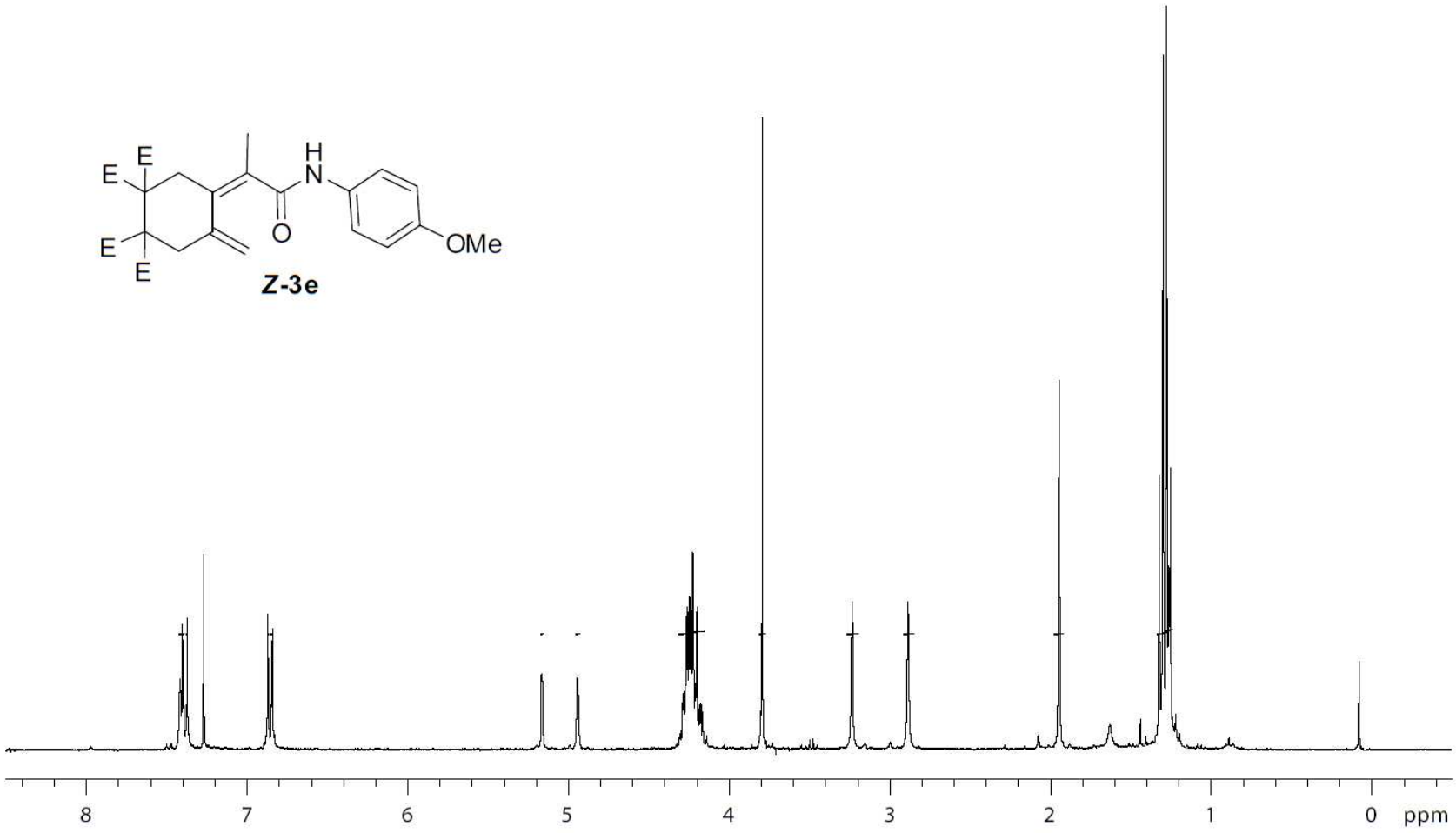
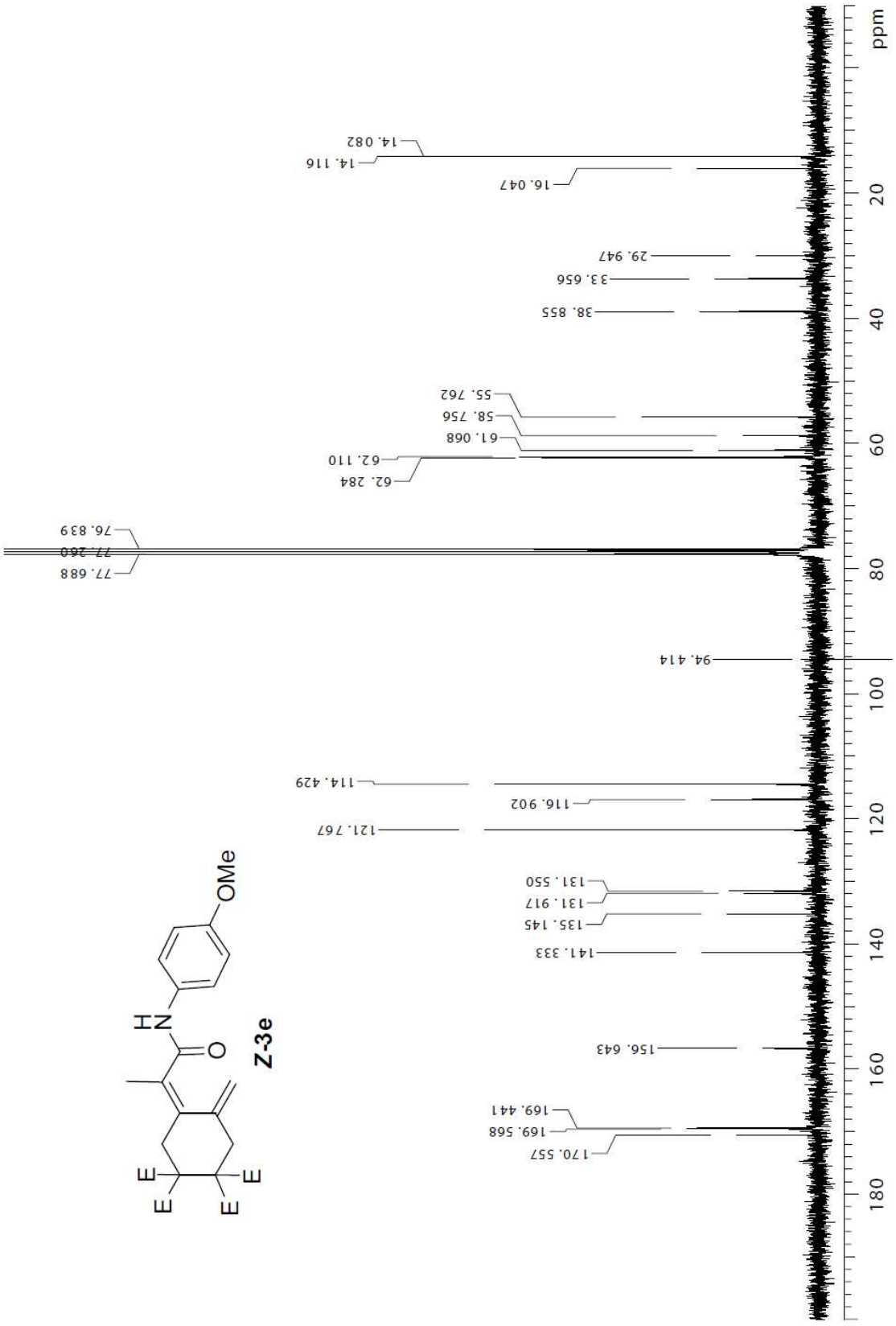
60
40
20
ppm



***E*-3e**



***Z*-3e**


ppm
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40
60
80
100
120
140
160
180
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16.047
29.947
33.656
38.855
55.762
58.756
61.068
62.110
62.284
76.839
77.260
77.688
94.414
114.429
116.902
121.767
131.550
131.917
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170.557
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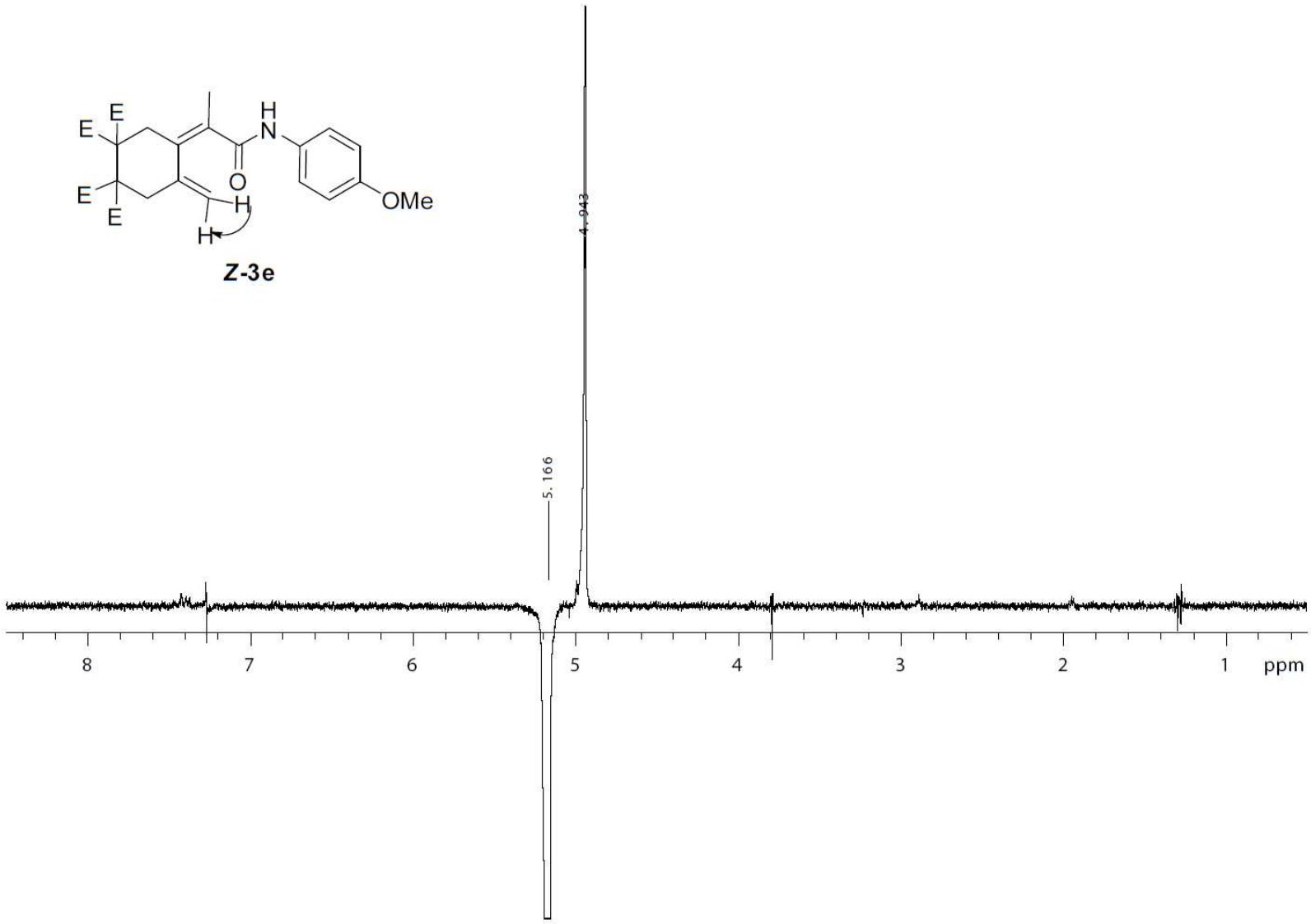
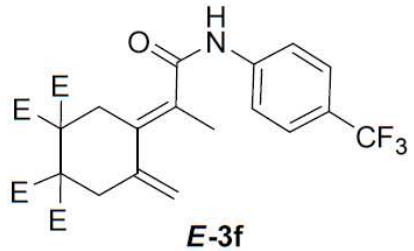
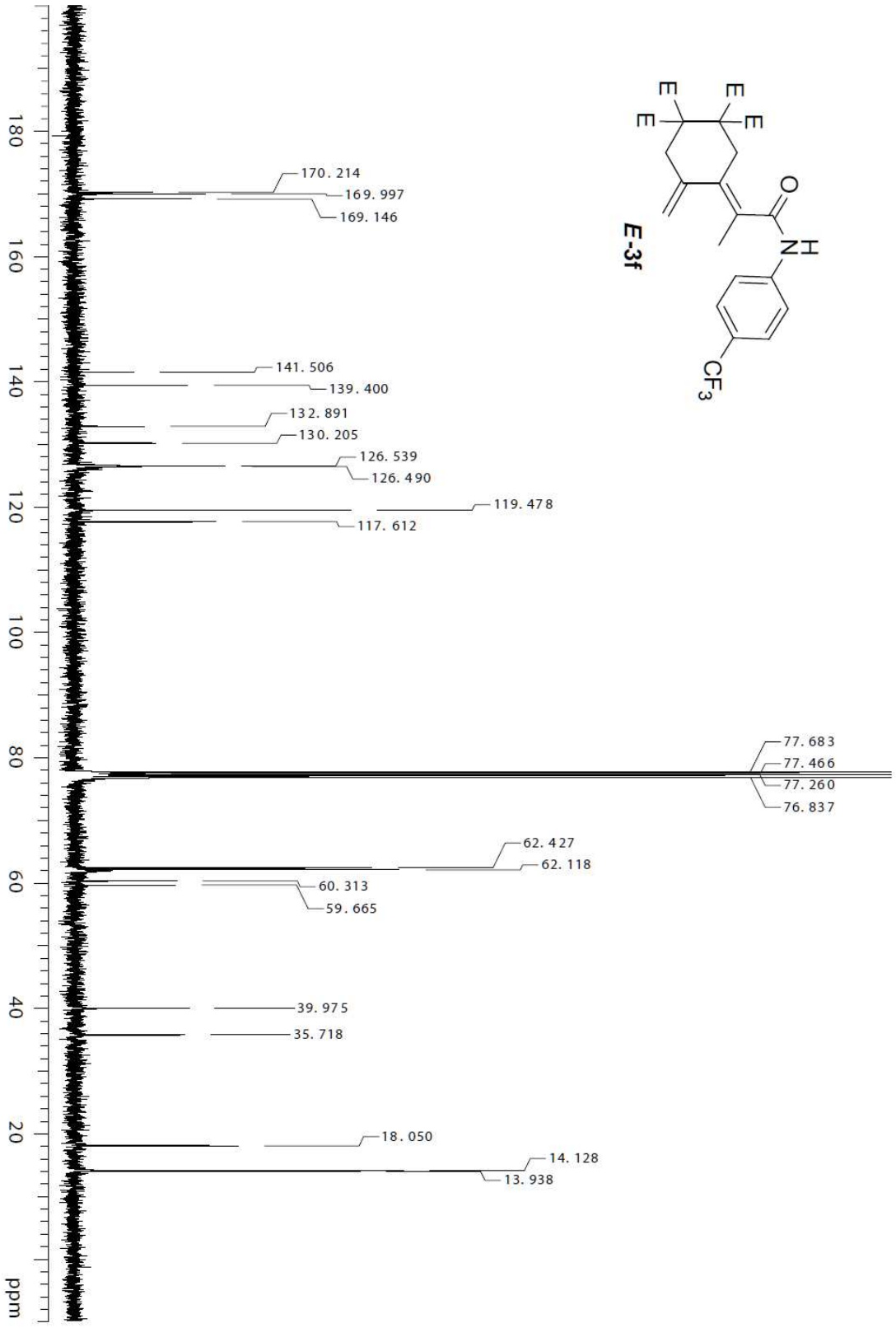
H
N
O
E
E
E
E
Z-3e

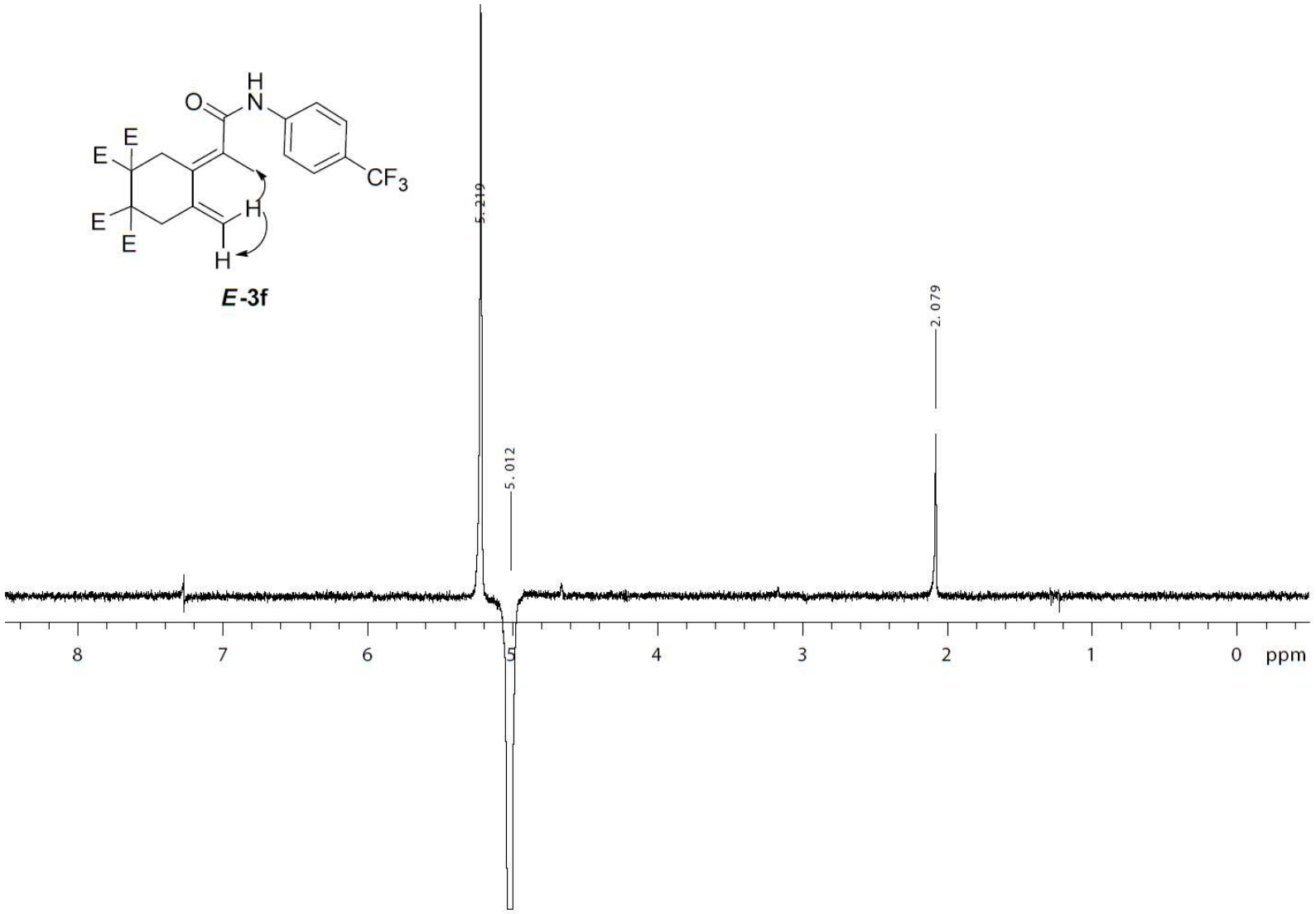

E
E
E
E
H
N
O
H
H
OMe
Z-3e
4.943
5.166
8
7
6
5
4
3
2
1
ppm



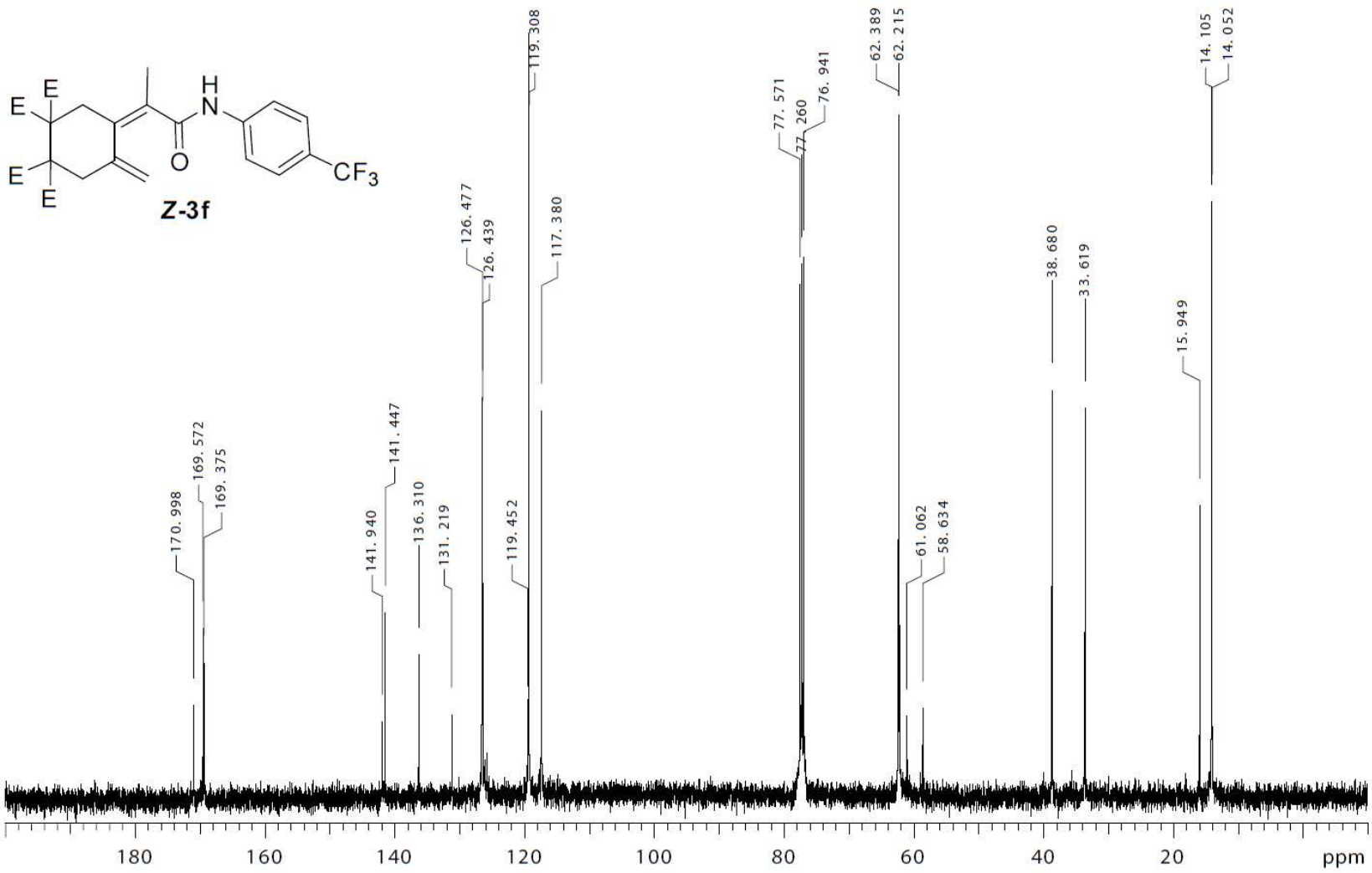
***E*-3f**

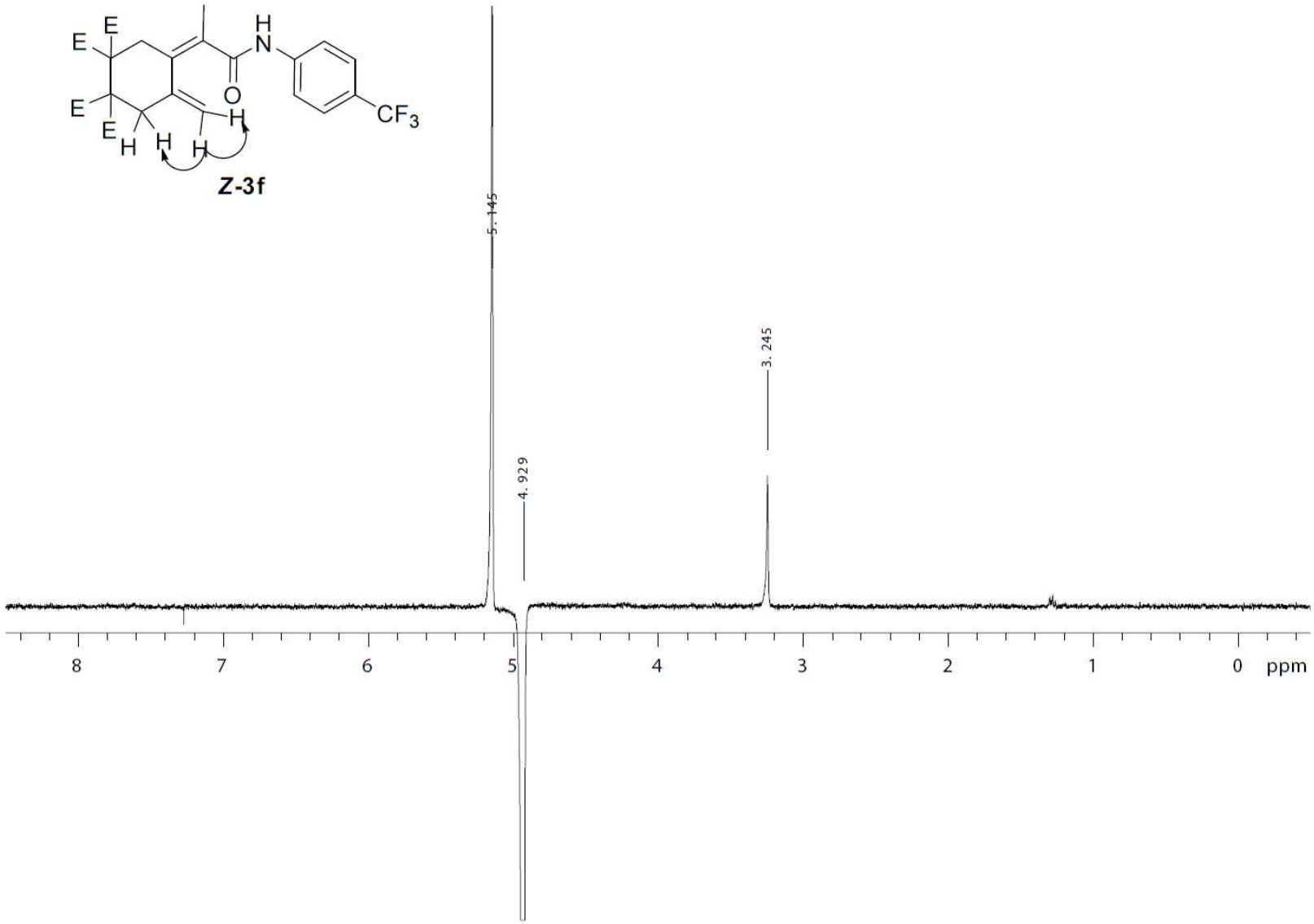
ccc

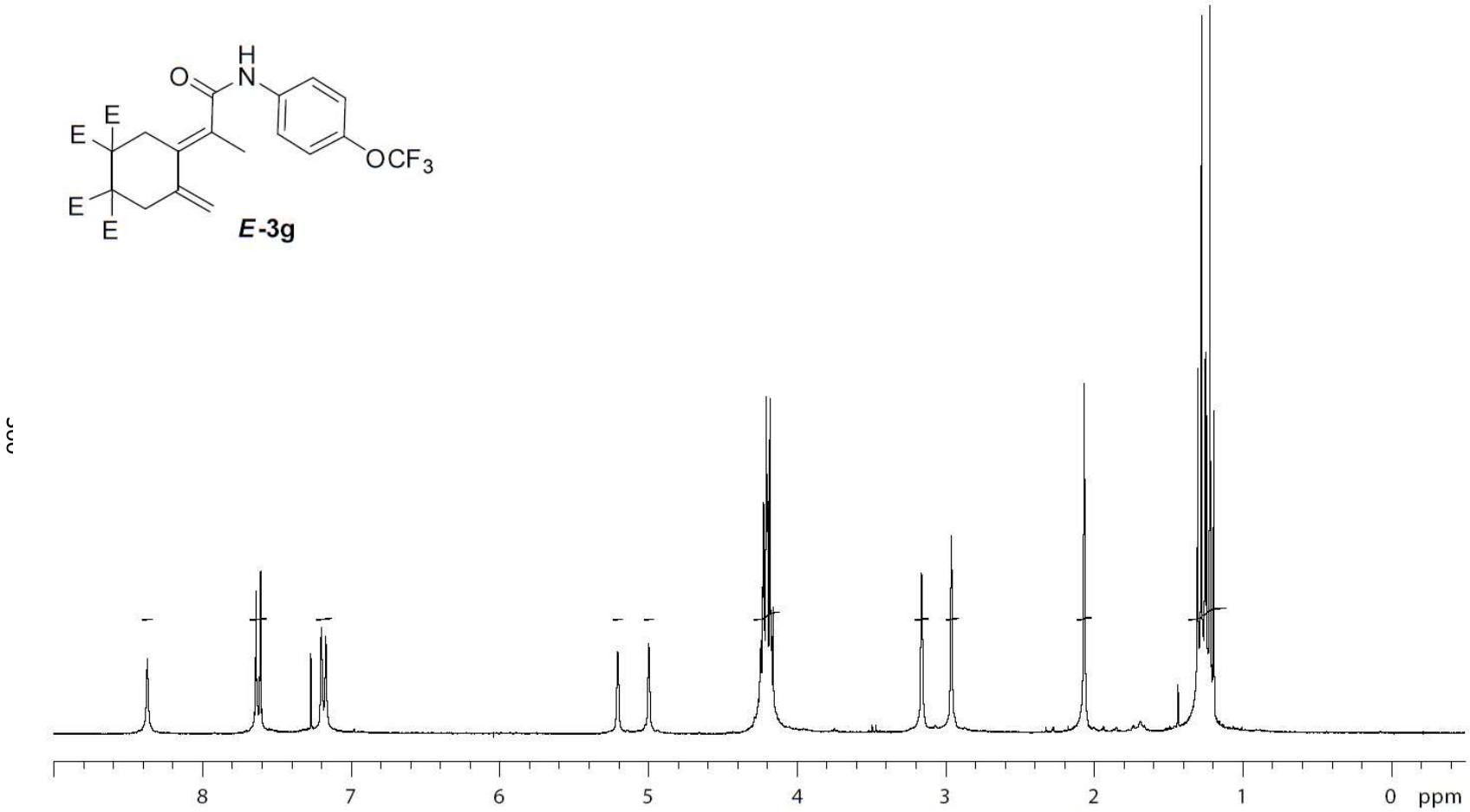

170.214
169.997
169.146
141.506
139.400
132.891
130.205
126.539
126.490
119.478
117.612
77.683
77.466
77.260
76.837
62.427
62.118
60.313
59.665
39.975
35.718
18.050
14.128
13.938
ppm
E-3f

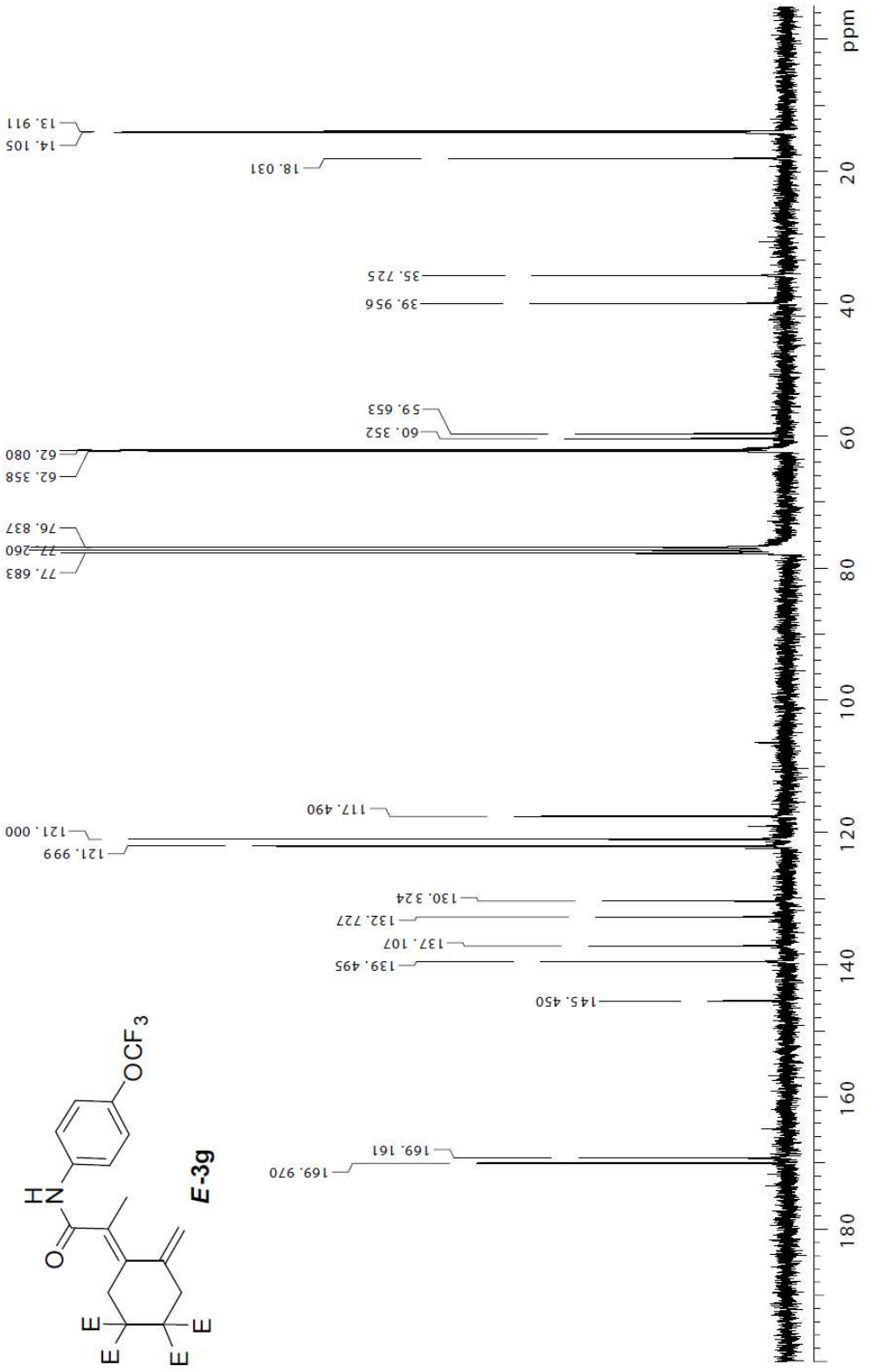

O
H
N
E
E
E
E
E
CF3
H
H
E-3f
5.219
5.012
2.079
8
7
6
5
4
3
2
1
0
ppm

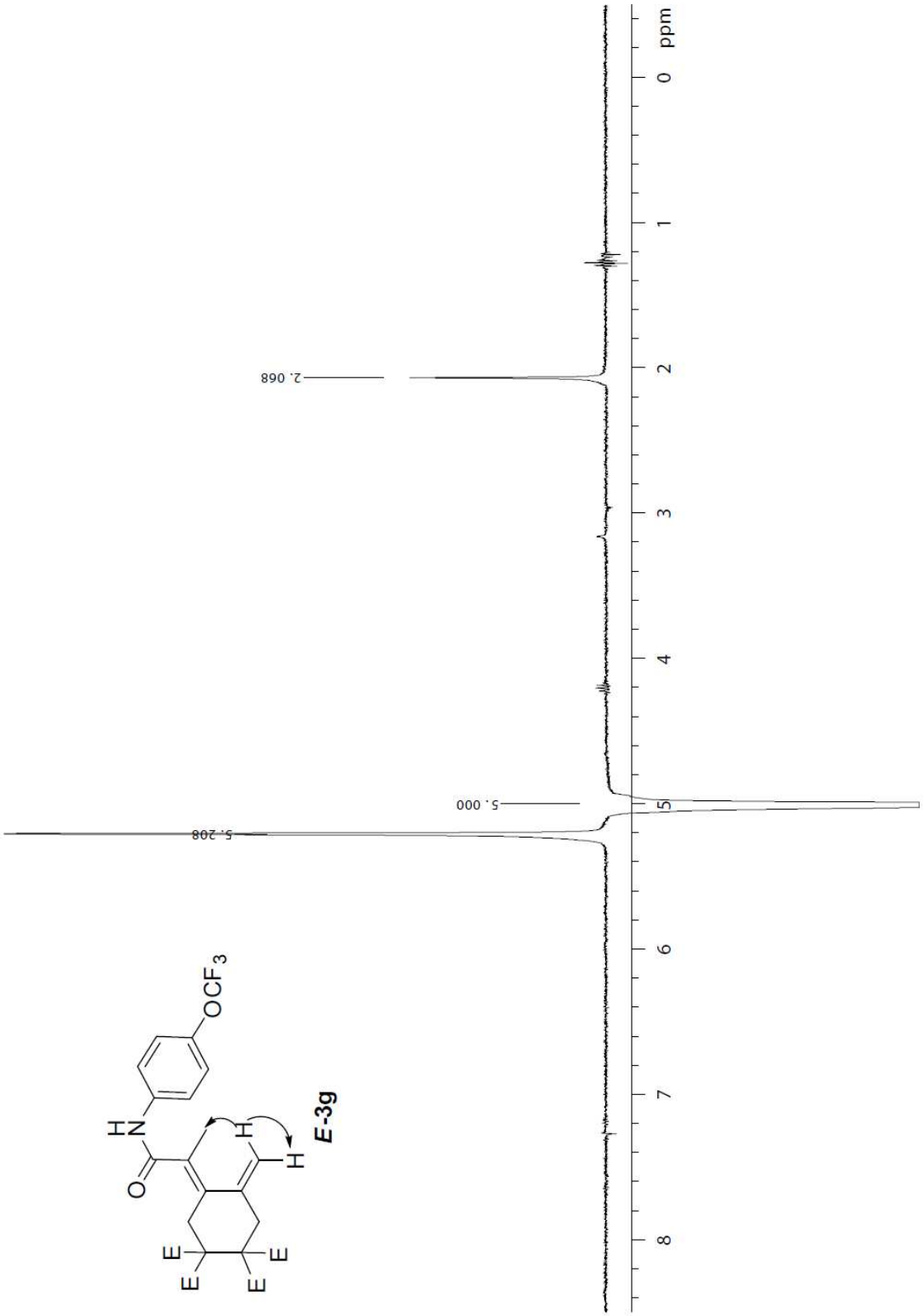
***Z*-3f**

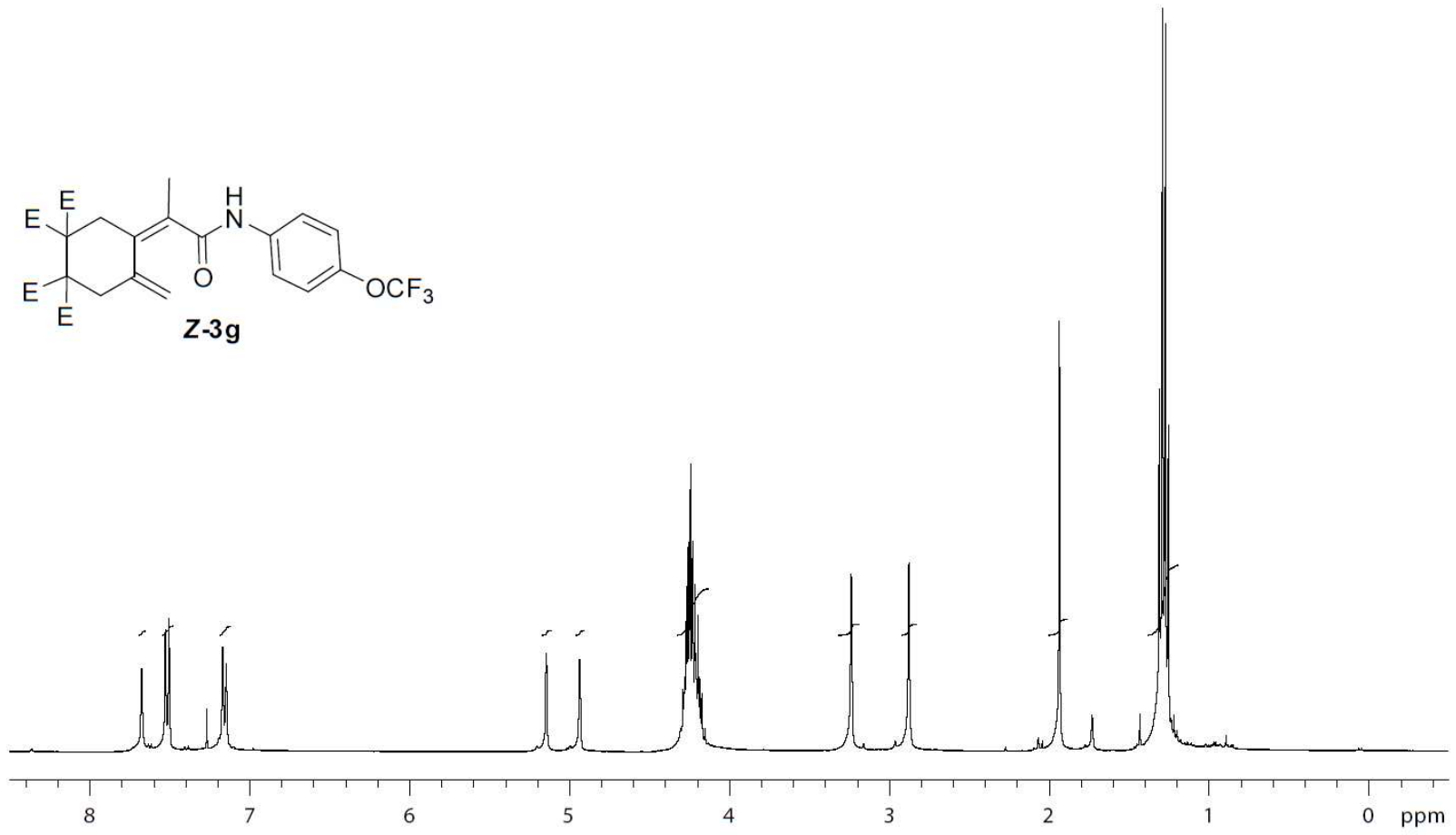

E
E
E
E
H
N
O
CF3
Z-3f
170.998
169.572
169.375
141.940
141.447
136.310
131.219
126.477
126.439
119.452
119.308
117.380
77.571
77.260
76.941
62.389
62.215
61.062
58.634
38.680
33.619
15.949
14.105
14.052
180
160
140
120
100
80
60
40
20
ppm

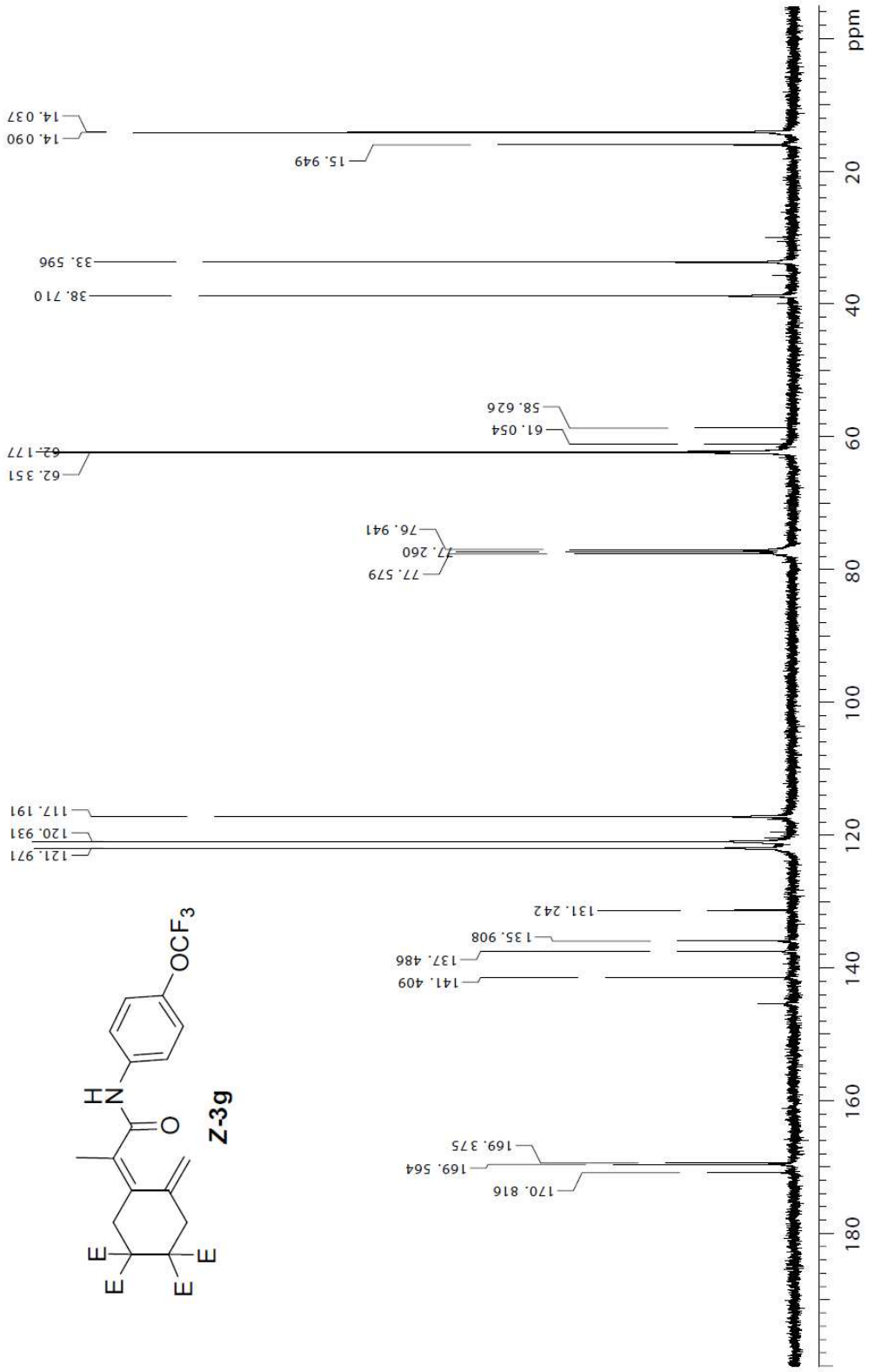

E
E
E
E
H
H
H
H
N
O
H
CF3
Z-3f
5.145
4.929
3.245
8
7
6
5
4
3
2
1
0
ppm


O
H
N
E
E
E
E
E
OCF3
E-3g
8
7
6
5
4
3
2
1
0
ppm

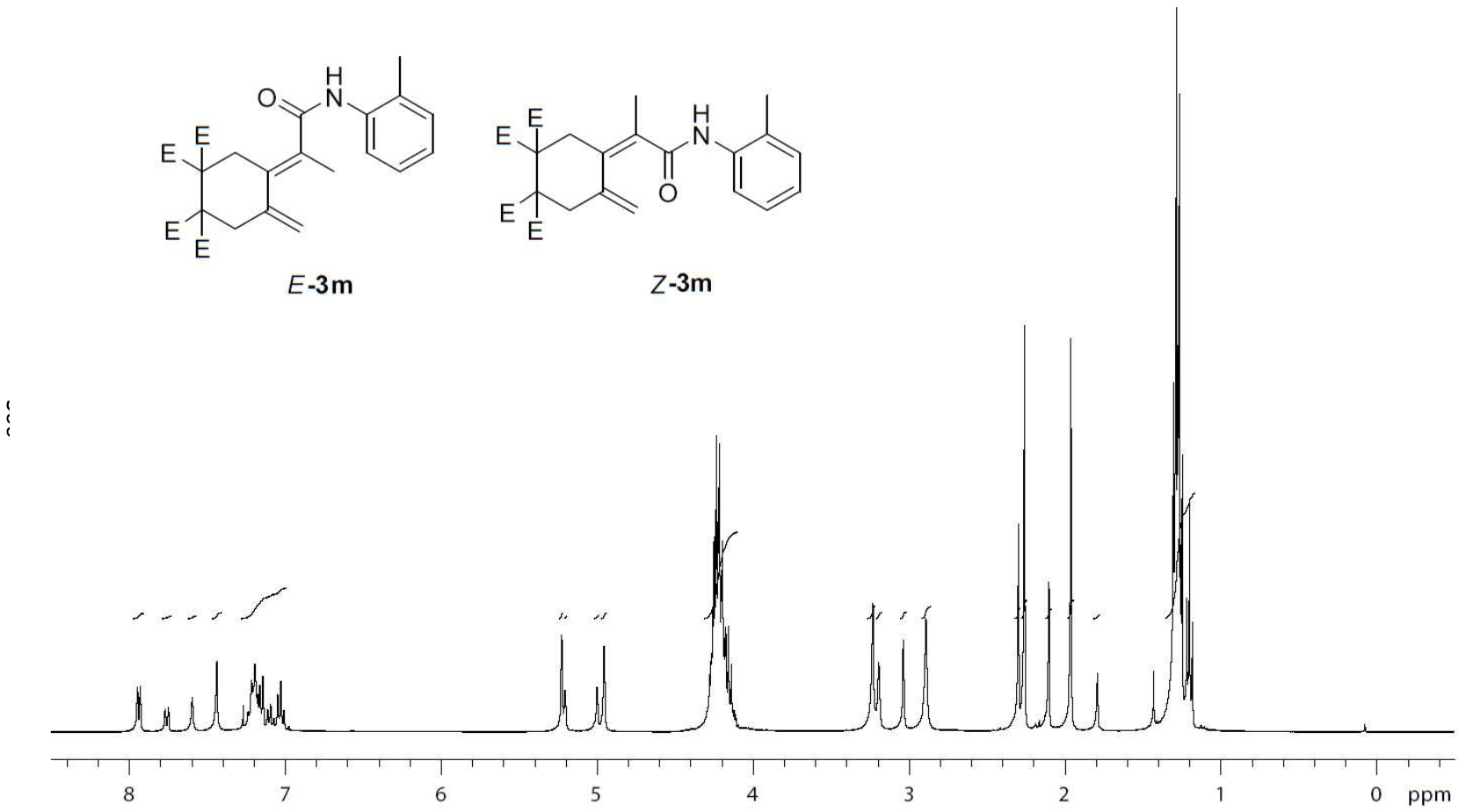

ppm
20
40
60
80
100
120
140
160
180
13.911
14.105
18.031
35.725
39.956
59.653
60.352
62.080
62.358
76.837
77.260
77.683
117.490
121.000
121.999
130.324
132.727
137.107
139.495
145.450
169.161
169.970
H
N
O
OCF3
E
E
E
E
E-3g


5.208
5.000
2.068
0
1
2
3
4
5
6
7
8
ppm
OCF3
H
N
O
H
H
E
E
E
E
E-3g


E
E
E
E
H
N
O
OCF3
Z-3g
8
7
6
5
4
3
2
1
0
ppm

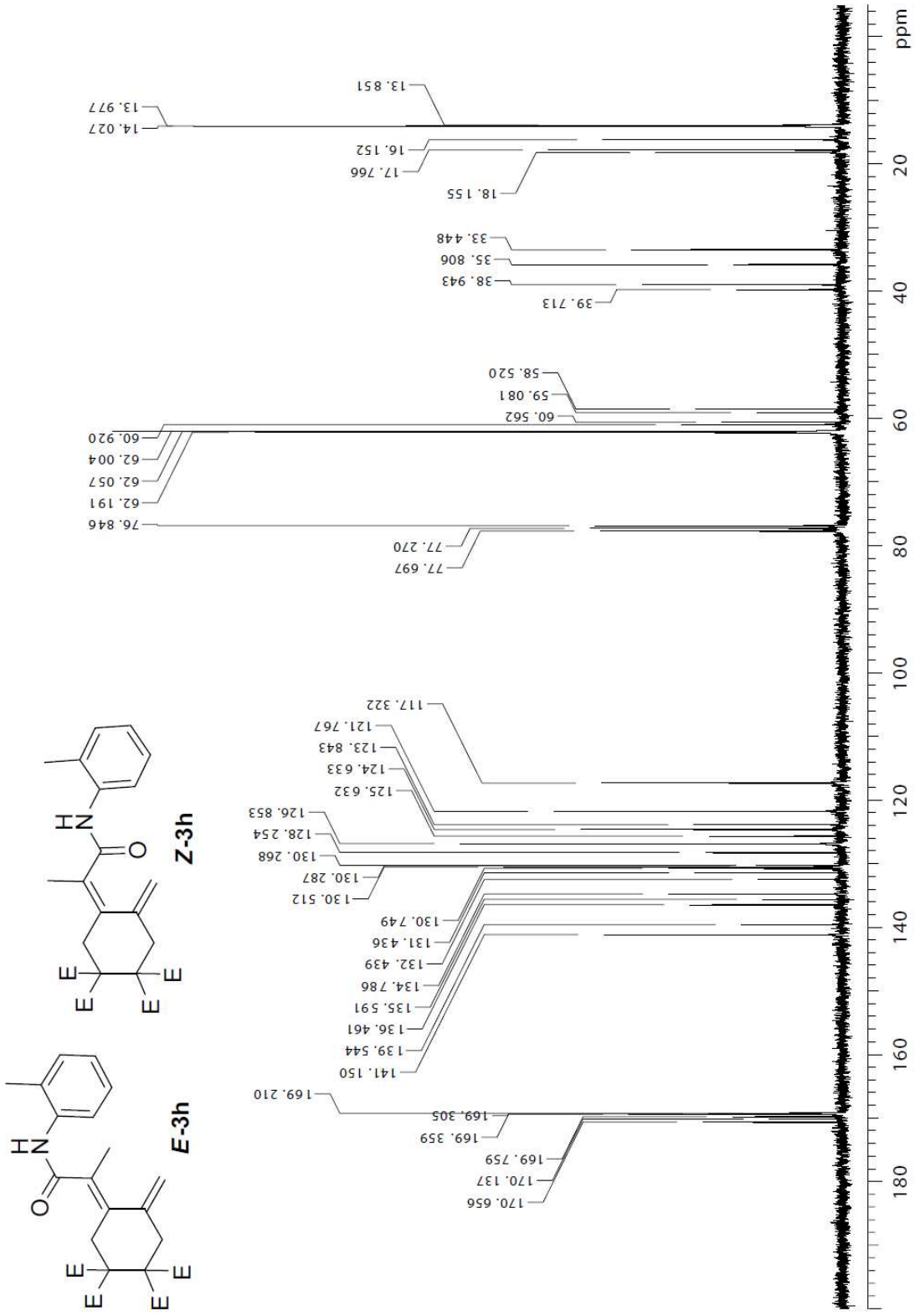

ppm
20
40
60
80
100
120
140
160
180
14.037
14.090
15.949
33.596
38.710
58.626
61.054
62.177
62.351
76.941
77.260
77.579
117.191
120.931
121.971
131.242
135.908
137.486
141.409
169.375
169.564
170.816
OCF3
H
N
O
E
E
E
E
Z-3g

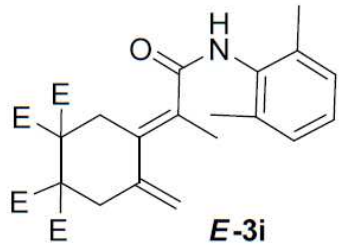
4.936
4.939
5.146
0
1
2
3
4
5
6
7
8
ppm
OCF3
H
N
O
H
H
E
E
E
E
Z-3g



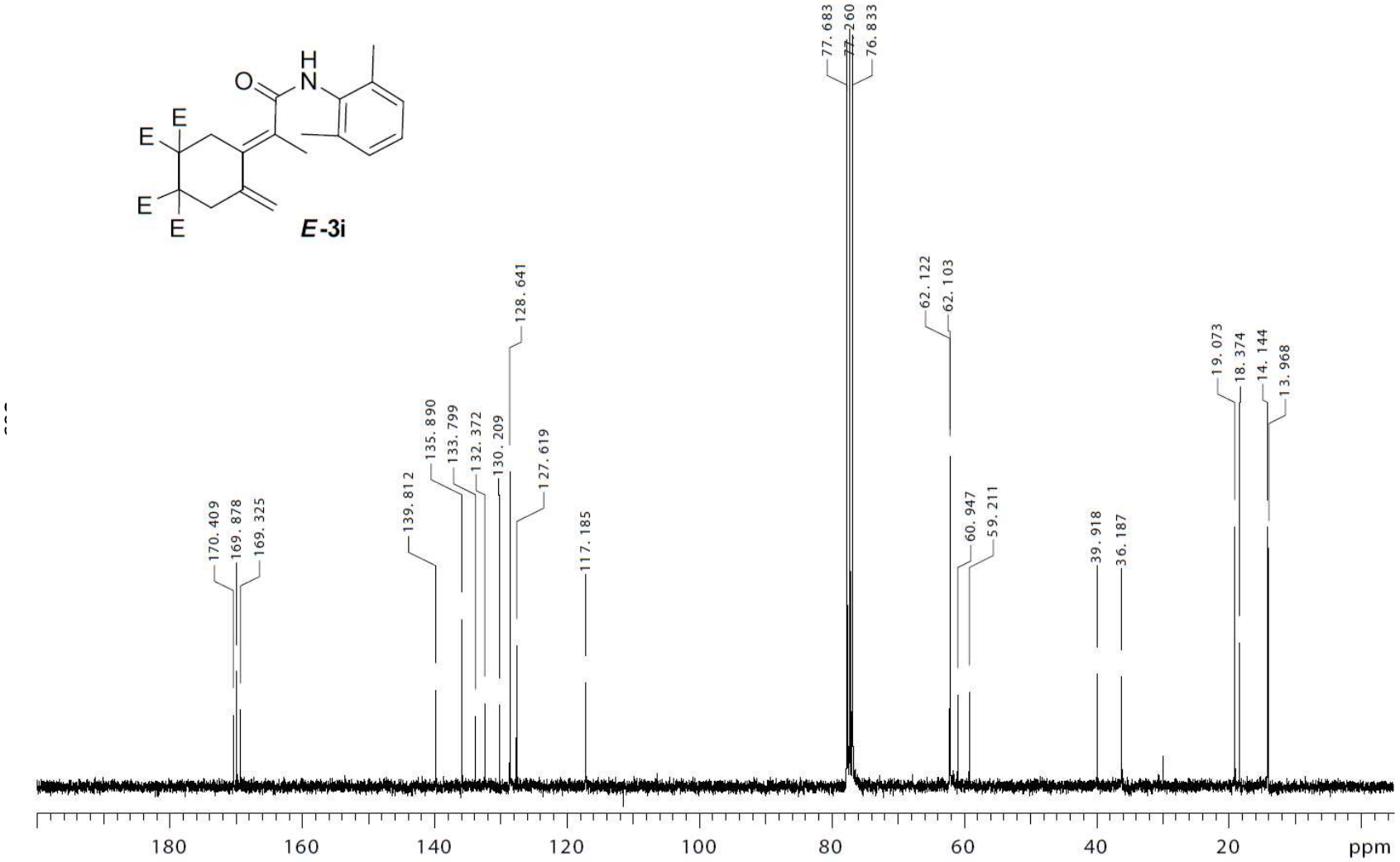
E-**3m**

Z-**3m**

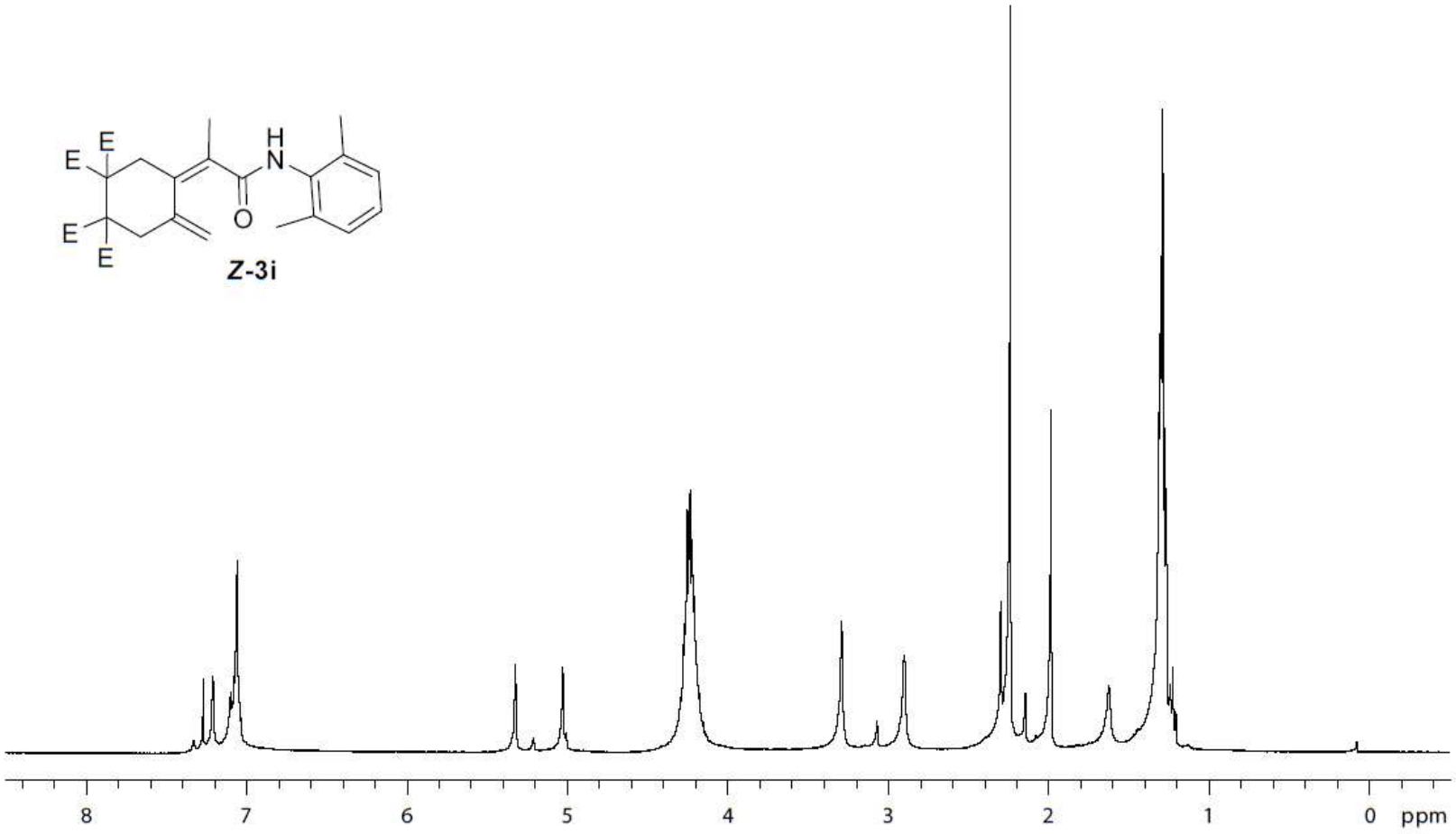

13.851
13.977
14.027
16.152
17.766
18.155
33.448
35.806
38.943
39.713
58.520
59.081
60.562
60.920
62.004
62.057
62.191
76.846
77.270
77.697
117.322
121.767
123.843
124.633
125.632
126.853
128.254
130.268
130.287
130.512
130.749
131.436
132.439
134.786
135.591
136.461
139.544
141.150
169.210
169.305
169.359
169.759
170.137
170.656
ppm
20
40
60
80
100
120
140
160
180
Z-3h
E-3h



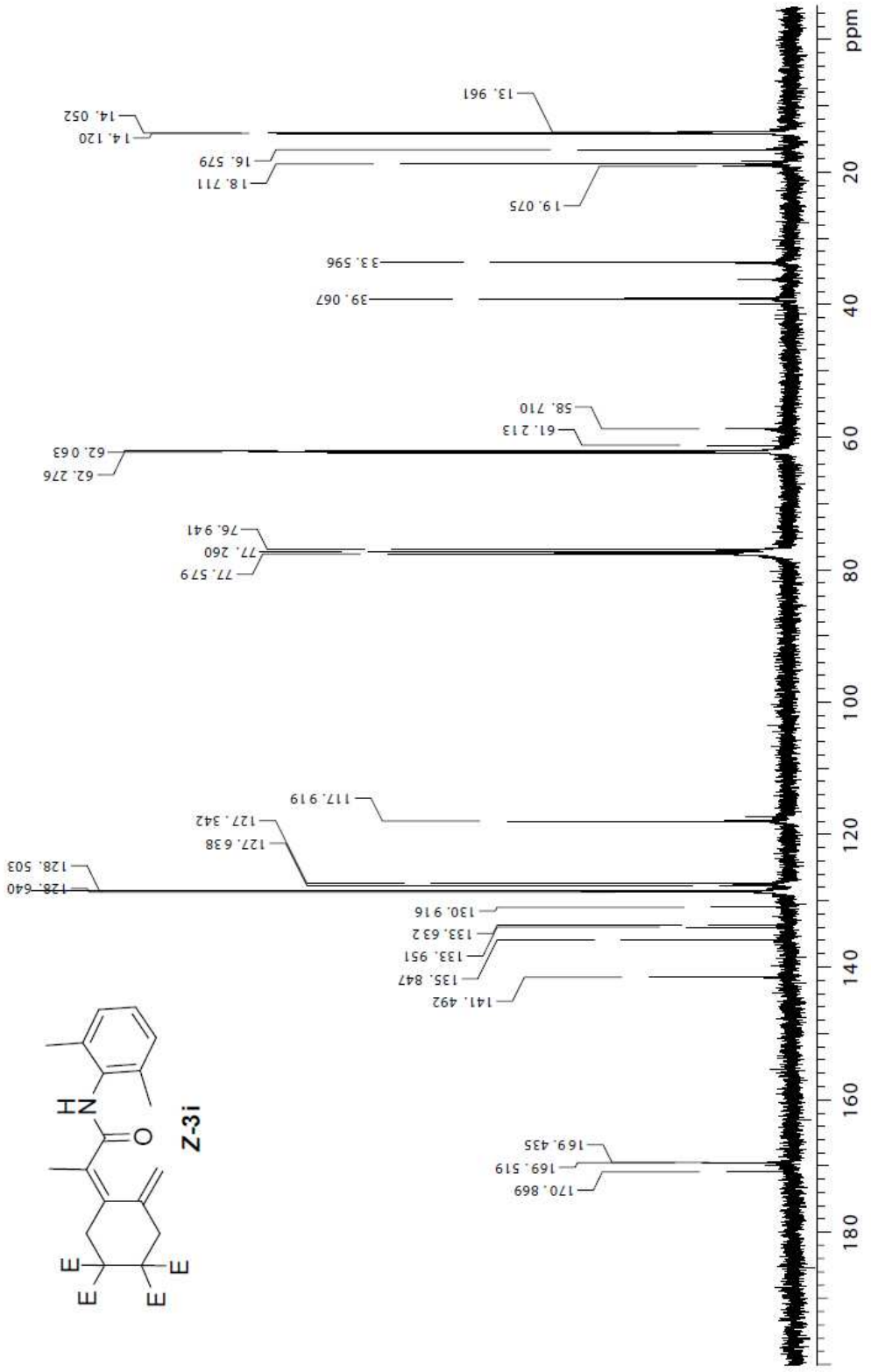
***E*-3i**

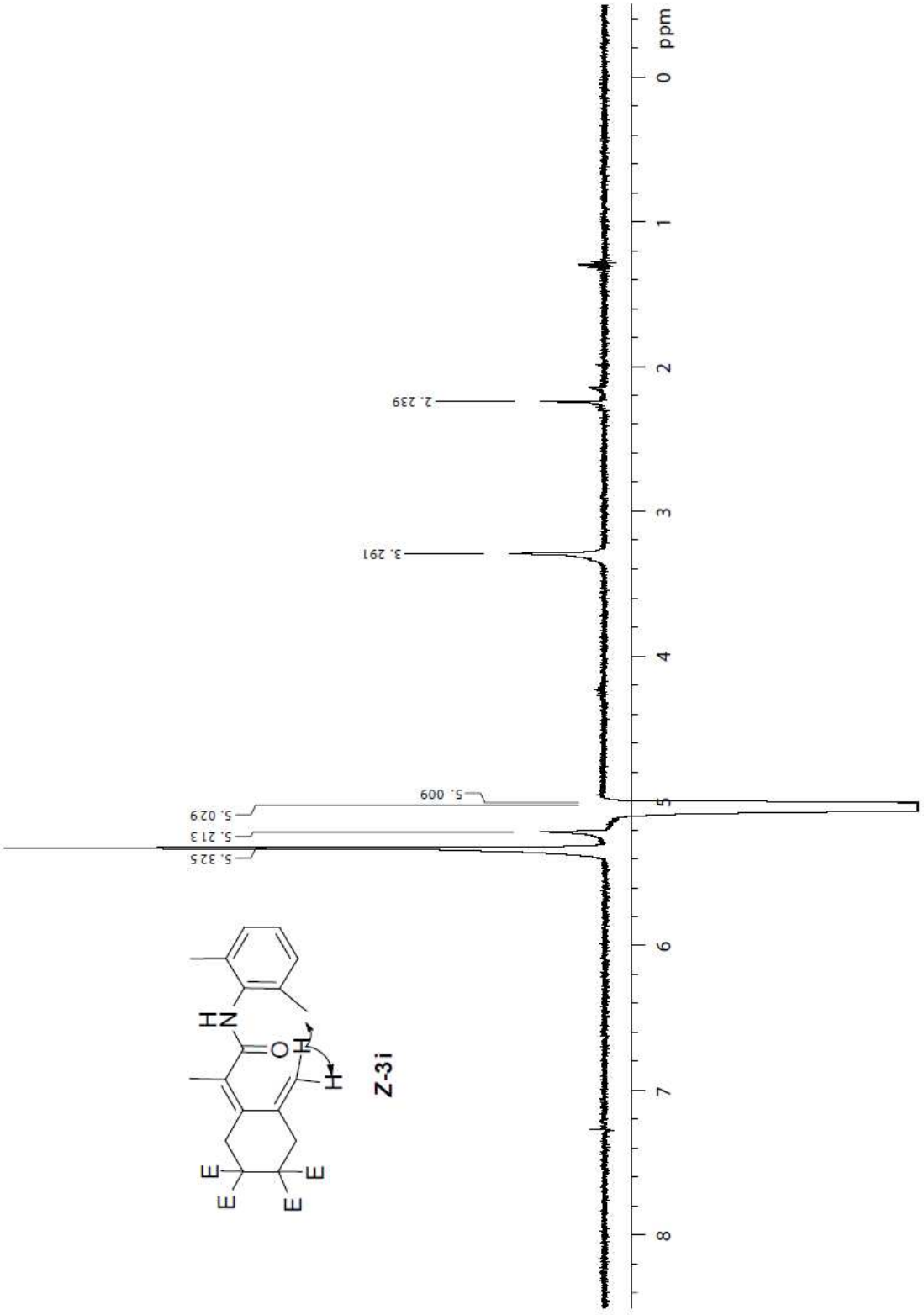

O
H
N
E
E
E
E
E
E-3i
170.409
169.878
169.325
139.812
135.890
133.799
132.372
130.209
128.641
127.619
117.185
77.683
77.260
76.833
62.122
62.103
60.947
59.211
39.918
36.187
19.073
18.374
14.144
13.968
180
160
140
120
100
80
60
40
20
ppm

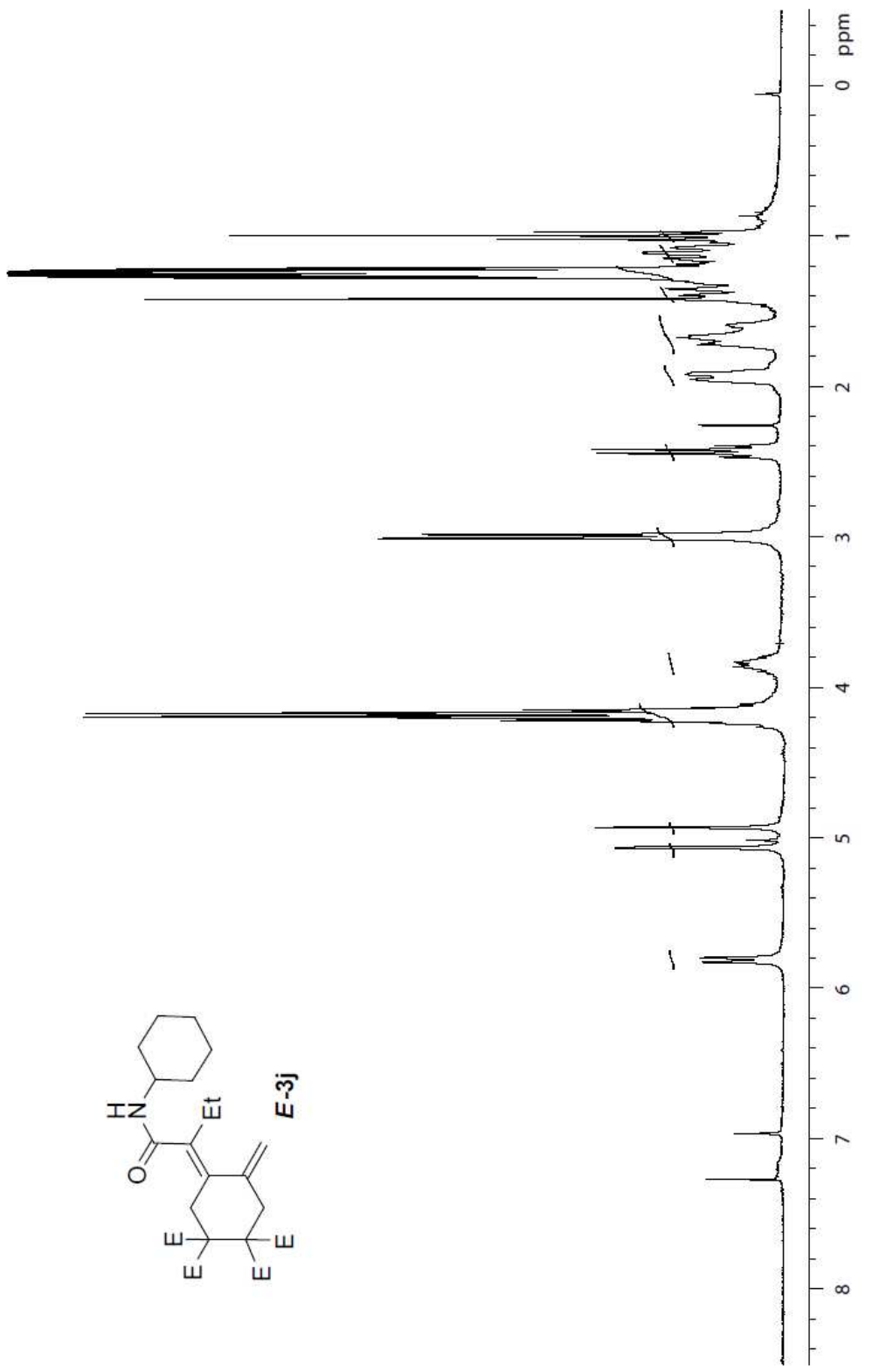
5.007
5.212
3.070
ppm
E-3i

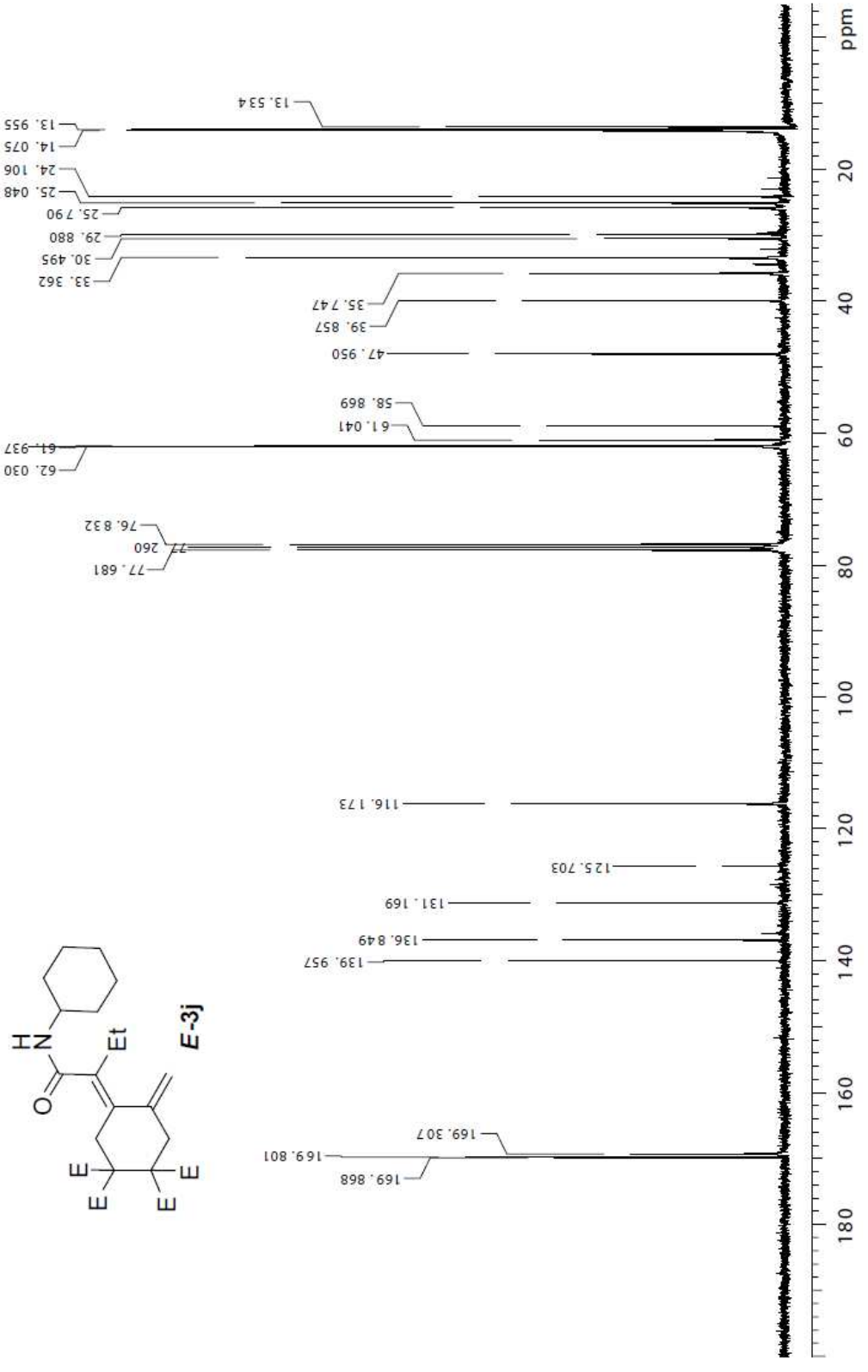


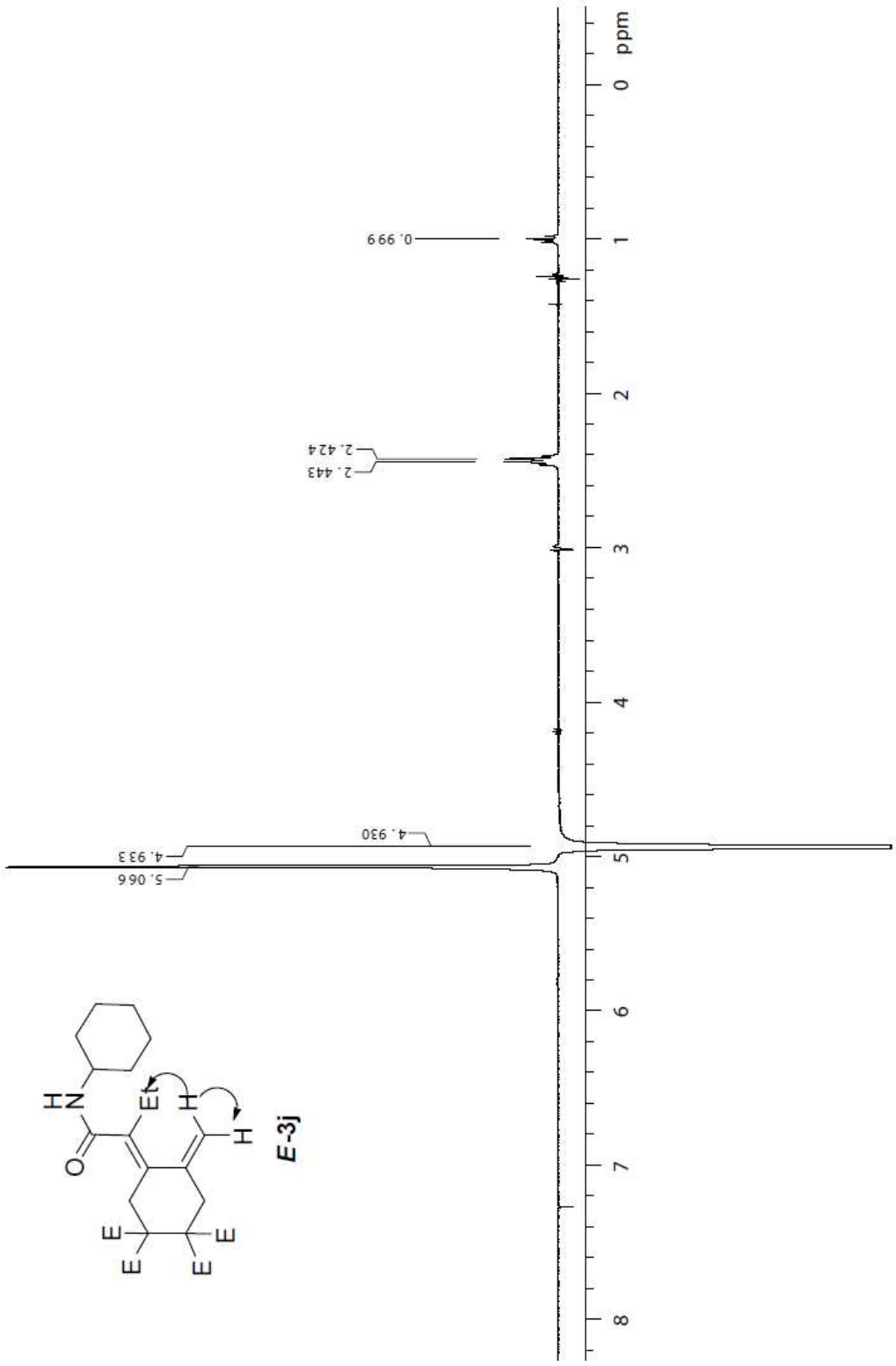
***Z*-3i**

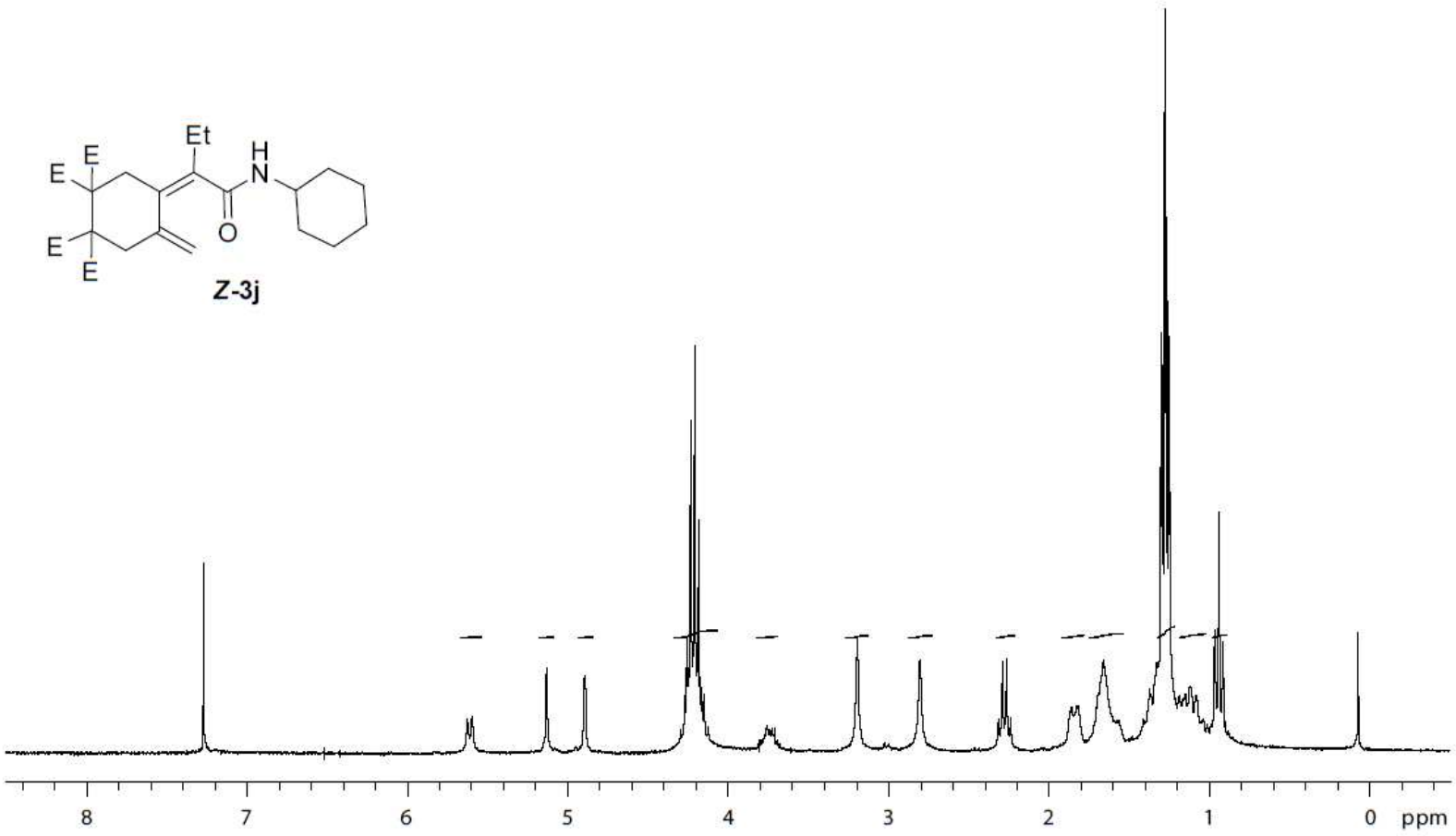

ppm
20
40
60
80
100
120
140
160
180
13.961
14.052
14.120
16.579
18.711
19.075
33.596
39.067
58.710
61.213
62.063
62.276
76.941
77.260
77.579
117.919
127.342
127.638
128.503
128.640
130.916
133.632
133.951
135.847
141.492
169.435
169.519
170.869
Z-3i

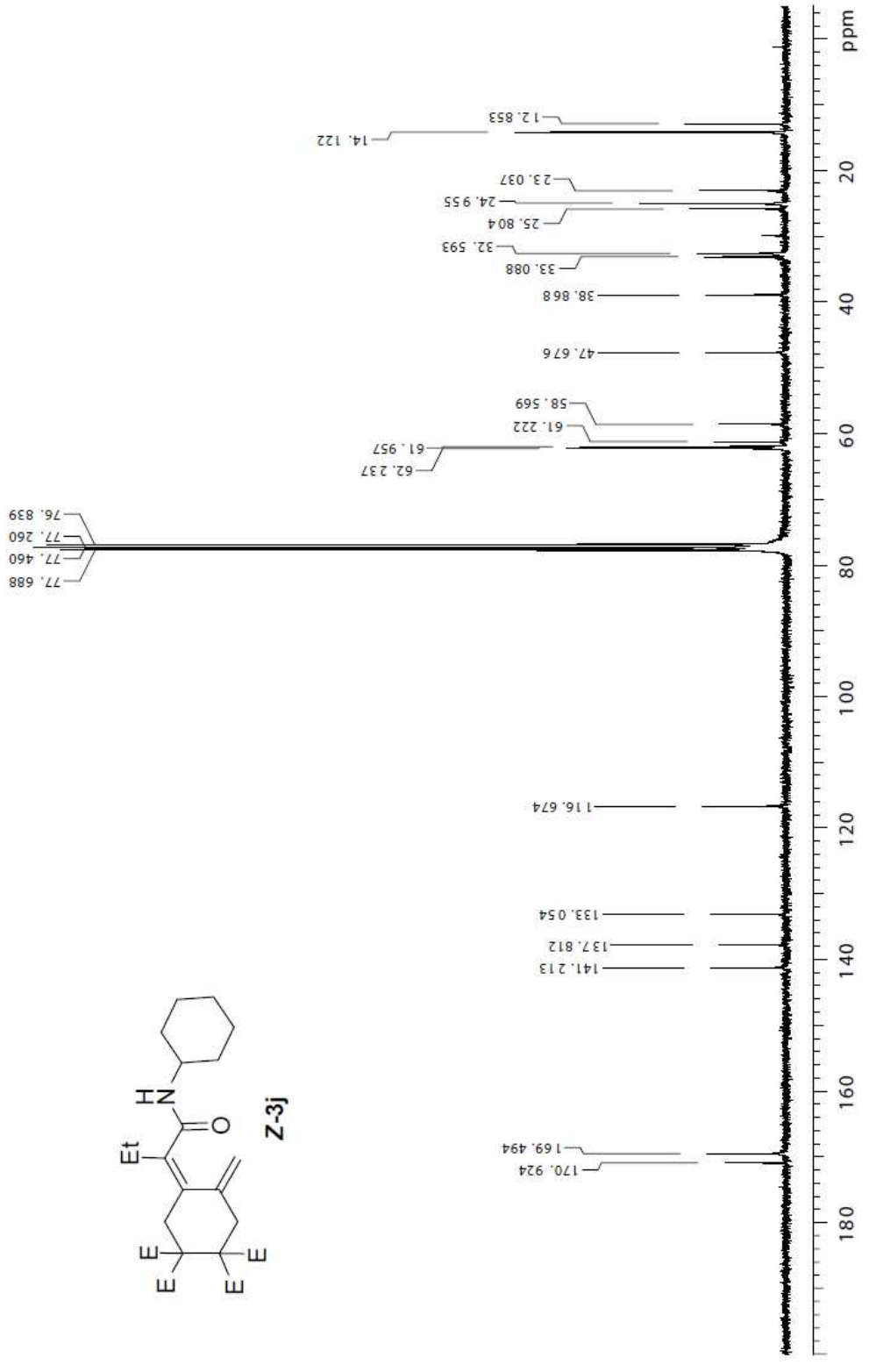

5.325
5.213
5.029
5.009
3.291
2.239
ppm
0
1
2
3
4
5
6
7
8
Z-3i


H
N
O
Et
E
E
E
E
E-3j
8
7
6
5
4
3
2
1
0
ppm

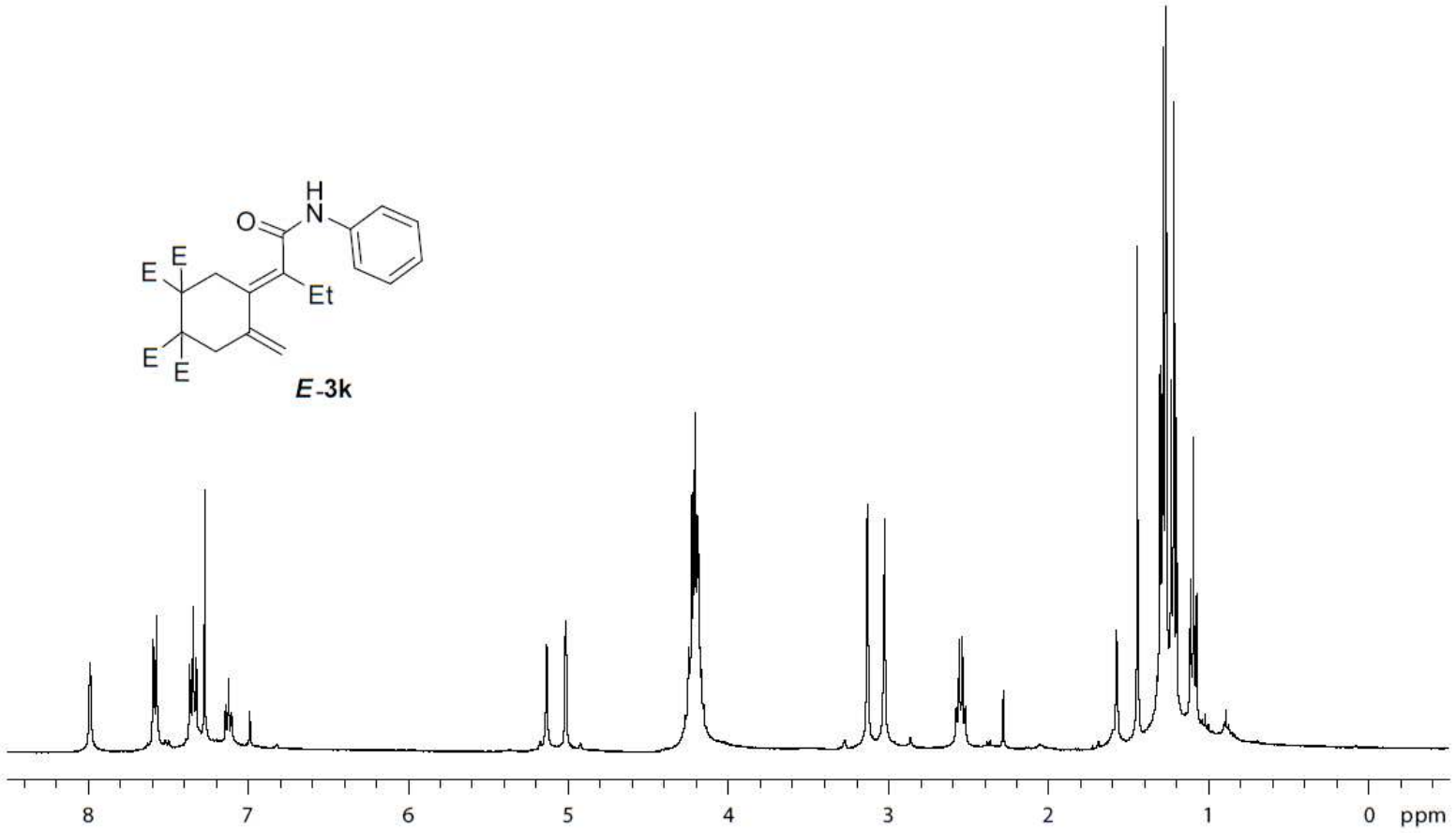

13.534
13.955
14.075
24.106
25.048
25.790
29.880
30.495
33.362
35.747
39.857
47.950
58.869
61.041
61.937
62.030
76.832
77.260
77.681
116.173
125.703
131.169
136.849
139.957
169.307
169.801
169.868
ppm
20
40
60
80
100
120
140
160
180
H
N
O
Et
E
E
E
E
E-3j


0. 999
2. 443
2. 424
4. 930
4. 933
5. 066
ppm
0
1
2
3
4
5
6
7
8
H
N
O
Et
H
H
E
E
E
E
E-3j

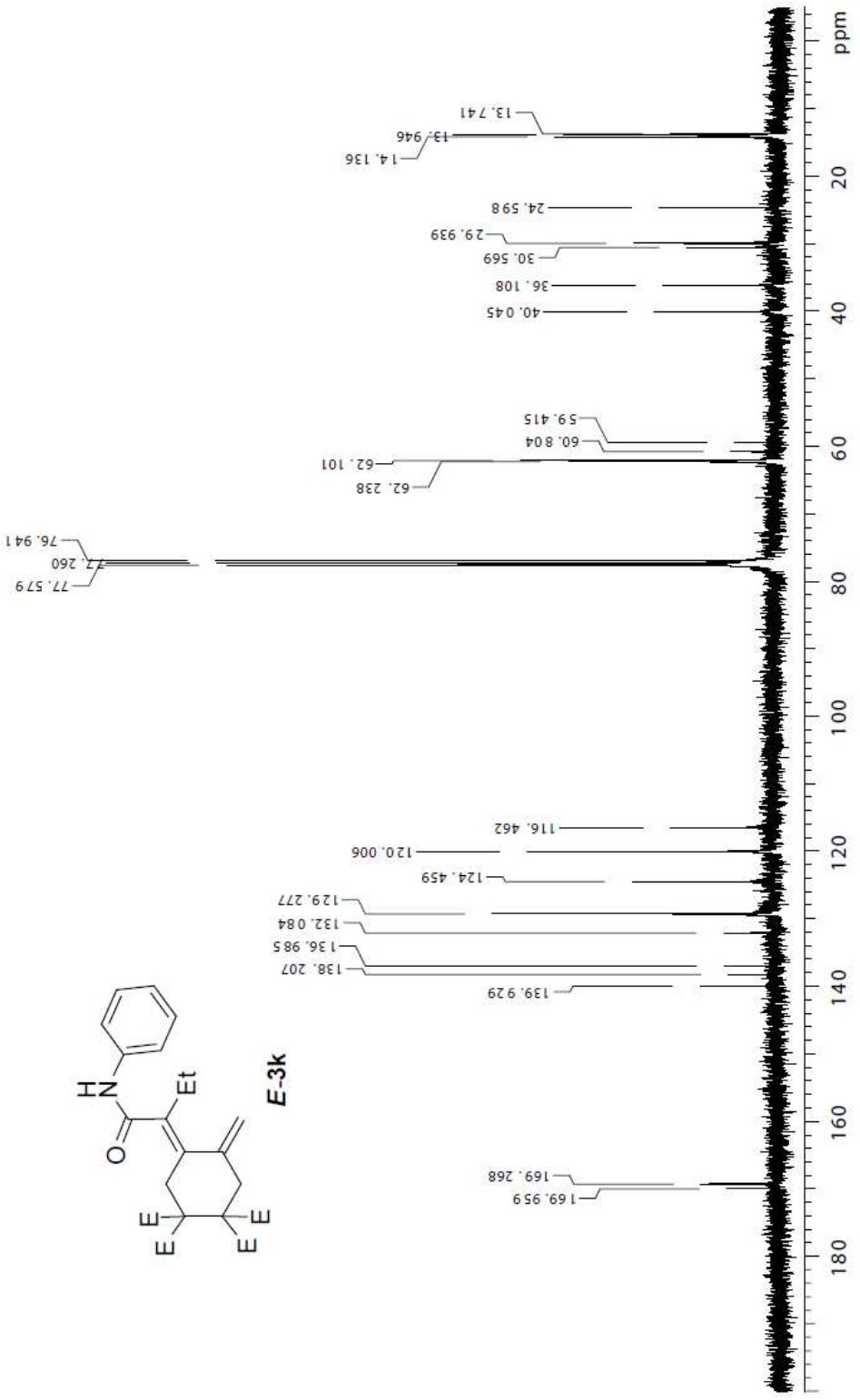

Et
E
E
E
E
H
N
O
Z-3j
8
7
6
5
4
3
2
1
0
ppm


Z-3j
Et
H
N
O
E
E
E
E
ppm
20
40
60
80
100
120
140
160
180
12.853
14.122
23.037
24.955
25.804
32.593
33.088
38.868
47.676
58.569
61.222
61.957
62.237
76.839
77.260
77.460
77.688
116.674
133.054
137.812
141.213
169.494
170.924

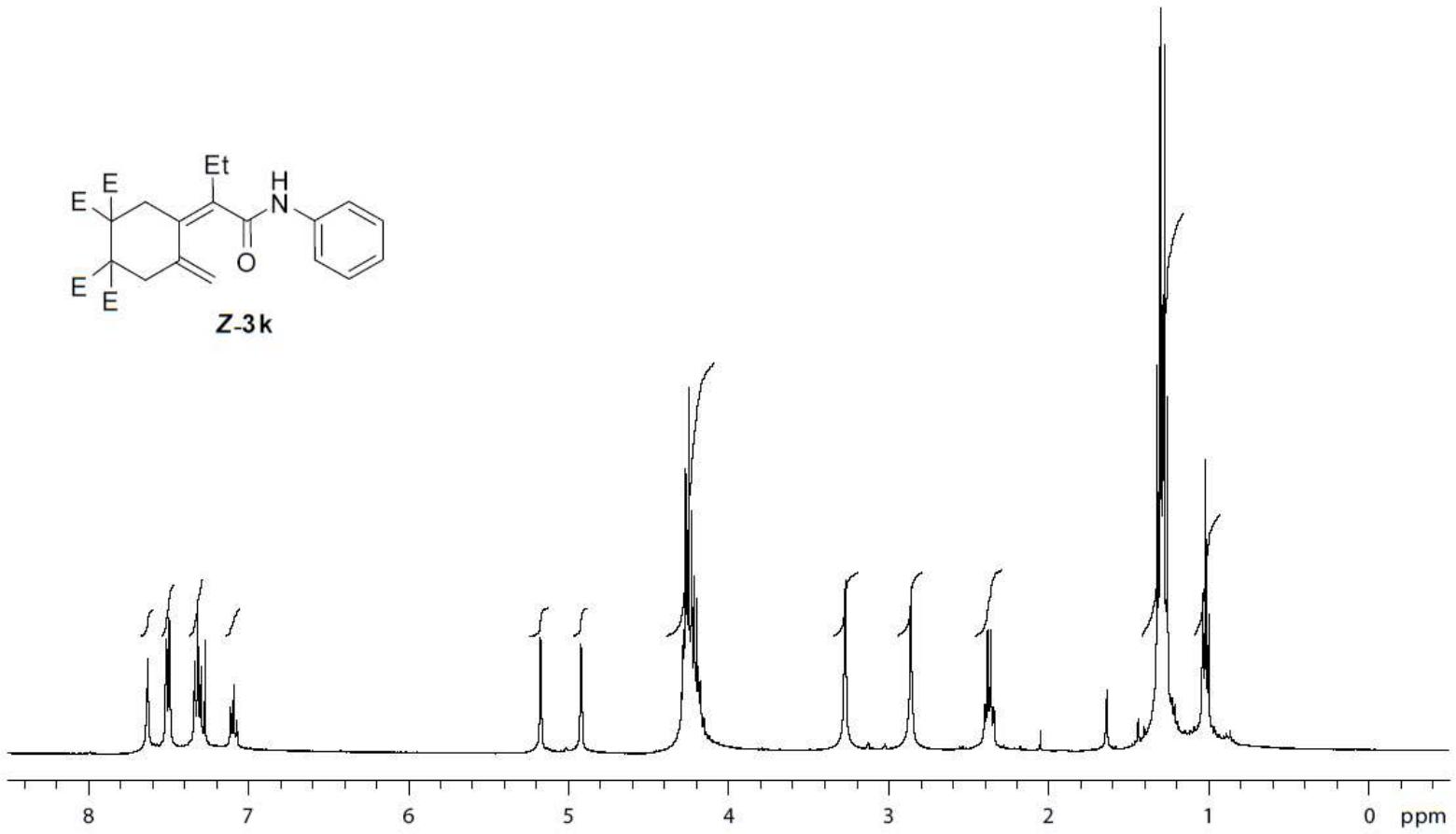
5.138
4.896
3.195
0
1
2
3
4
5
6
7
8
ppm
Et
H
N
O
H
H
H
E
E
E
E
Z-3j

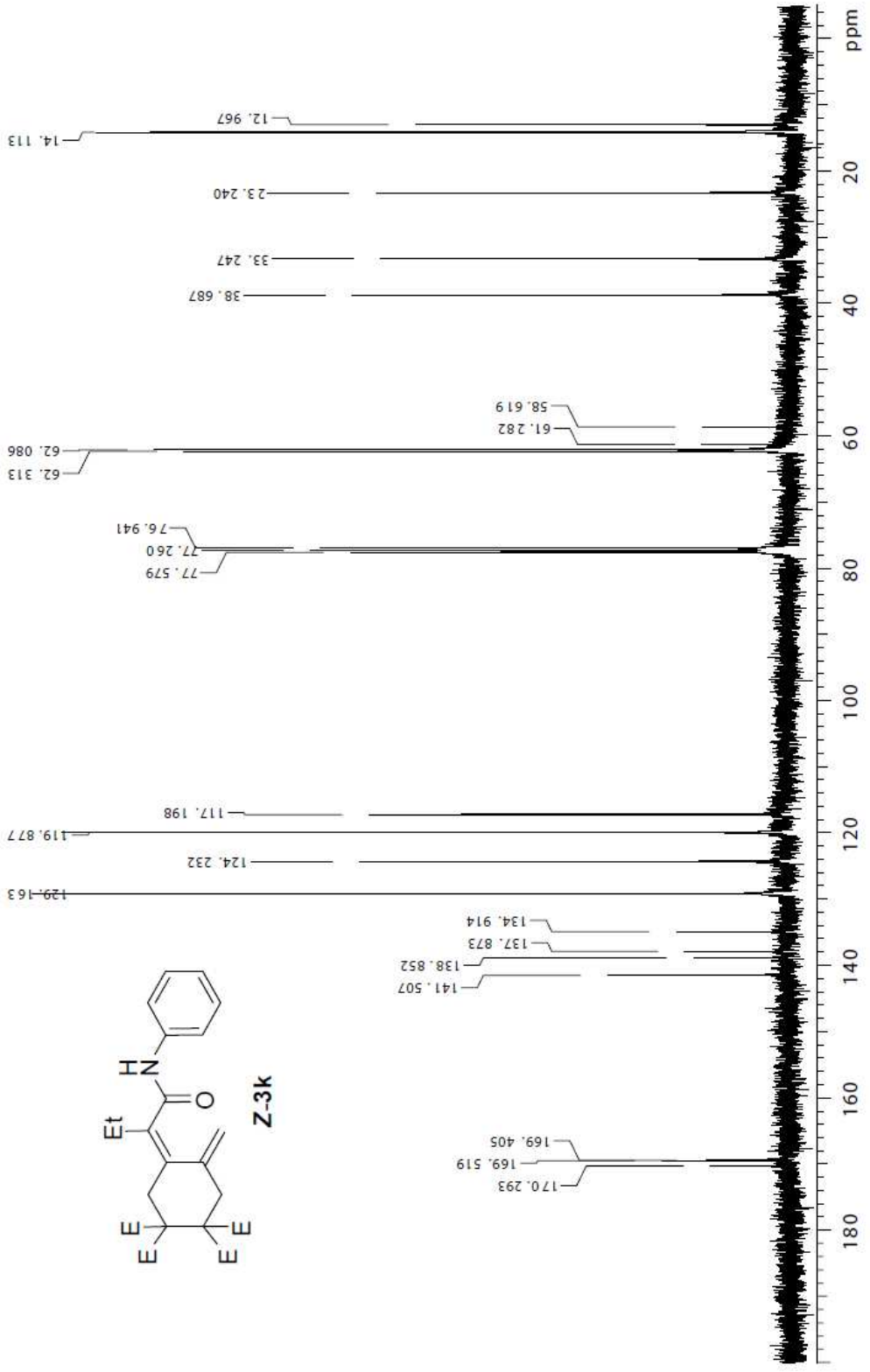


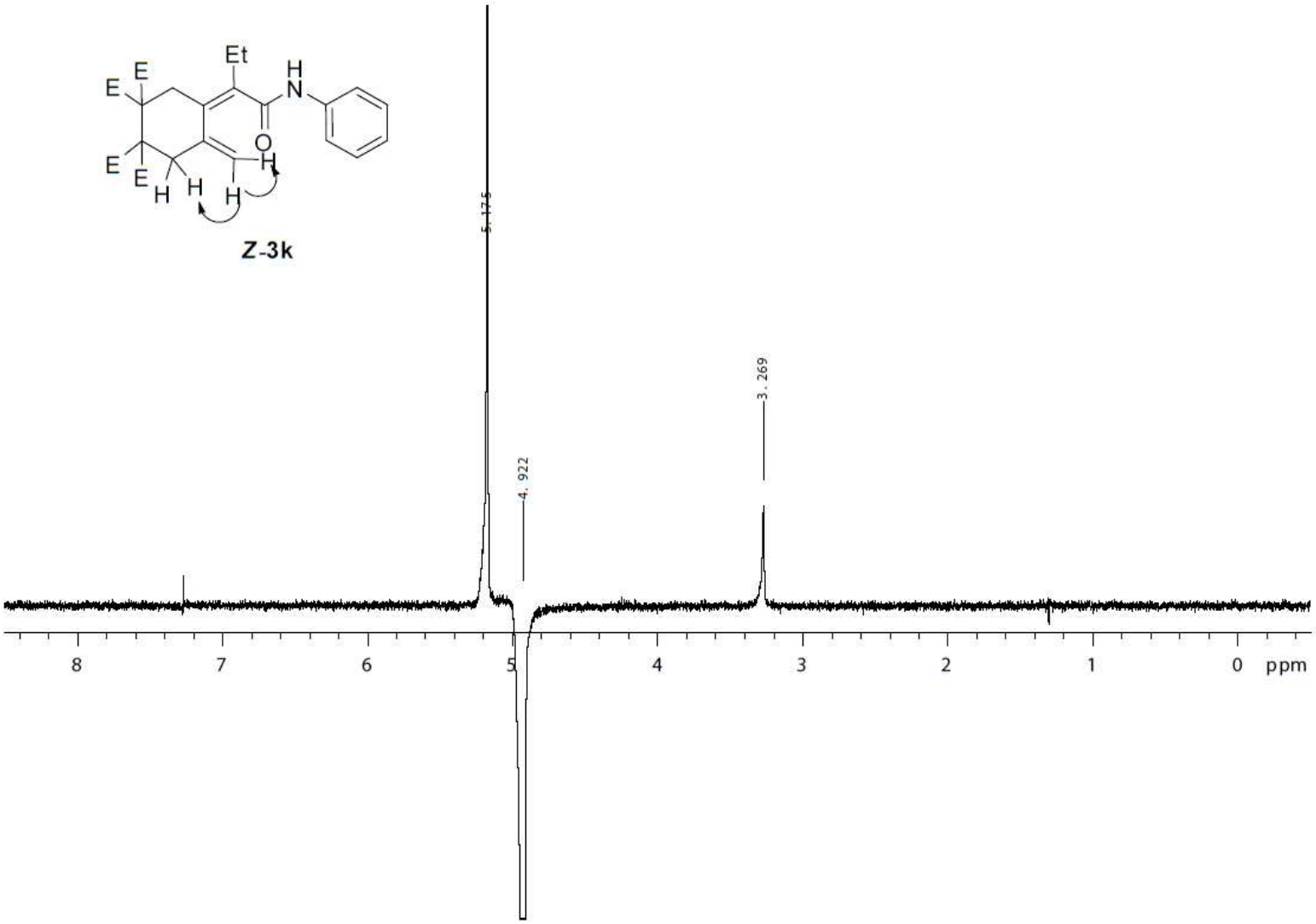
***E*-3k**

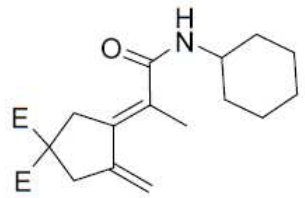

13.741
13.946
14.136
24.598
29.939
30.569
36.108
40.045
59.415
60.804
62.101
62.238
76.941
77.260
77.579
116.462
120.006
124.459
129.277
132.084
136.985
138.207
139.929
169.268
169.959
ppm
20
40
60
80
100
120
140
160
180
E-3k
Et
H
N
O
E
E
E
E

7.269
5.136
5.016
2.557
2.537
1.574
1.443
1.093
ppm
E-3k

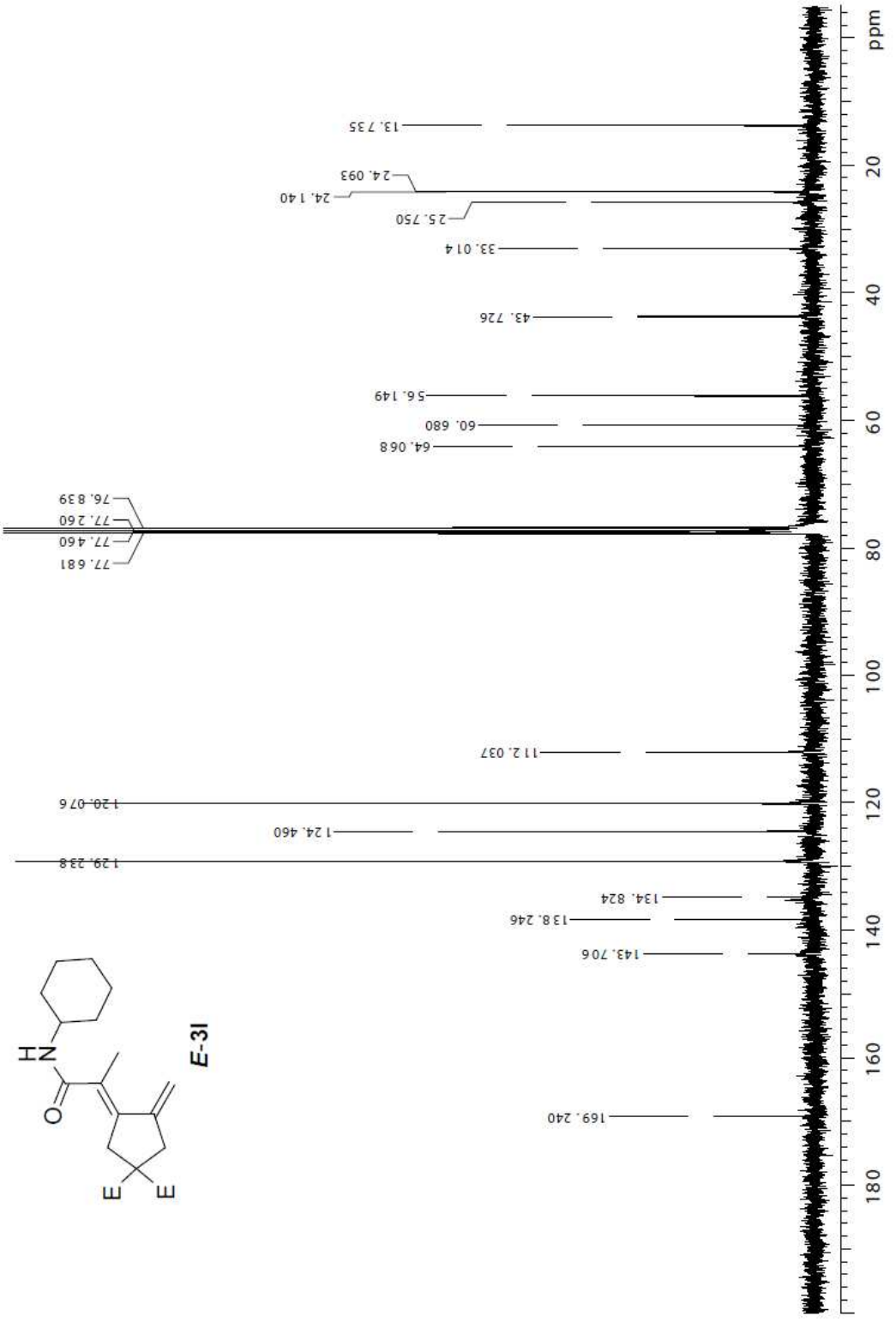

Et
E
E
H
N
O
E
E
Z-3k
8
7
6
5
4
3
2
1
0
ppm


ppm
20
40
60
80
100
120
140
160
180
12.967
14.113
23.240
33.247
38.687
58.619
61.282
62.086
62.313
76.941
77.260
77.579
117.198
119.877
124.232
129.163
134.914
137.873
138.852
141.507
169.405
169.519
170.293
Et
E
E
E
E
Z-3k

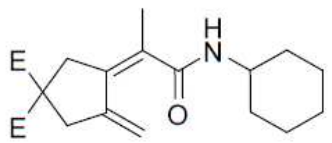

Et
E
E
E
E
H
N
O
H
H
H
H
Z-3k
5.175
4.922
3.269
8
7
6
5
4
3
2
1
0
ppm



E-3l


ppm
20
40
60
80
100
120
140
160
180
13.735
24.093
24.140
25.750
33.014
43.726
56.149
60.680
64.068
76.839
77.260
77.460
77.681
112.037
120.076
124.460
129.238
134.824
138.246
143.706
169.240
E
E
O
H
N
E-3l

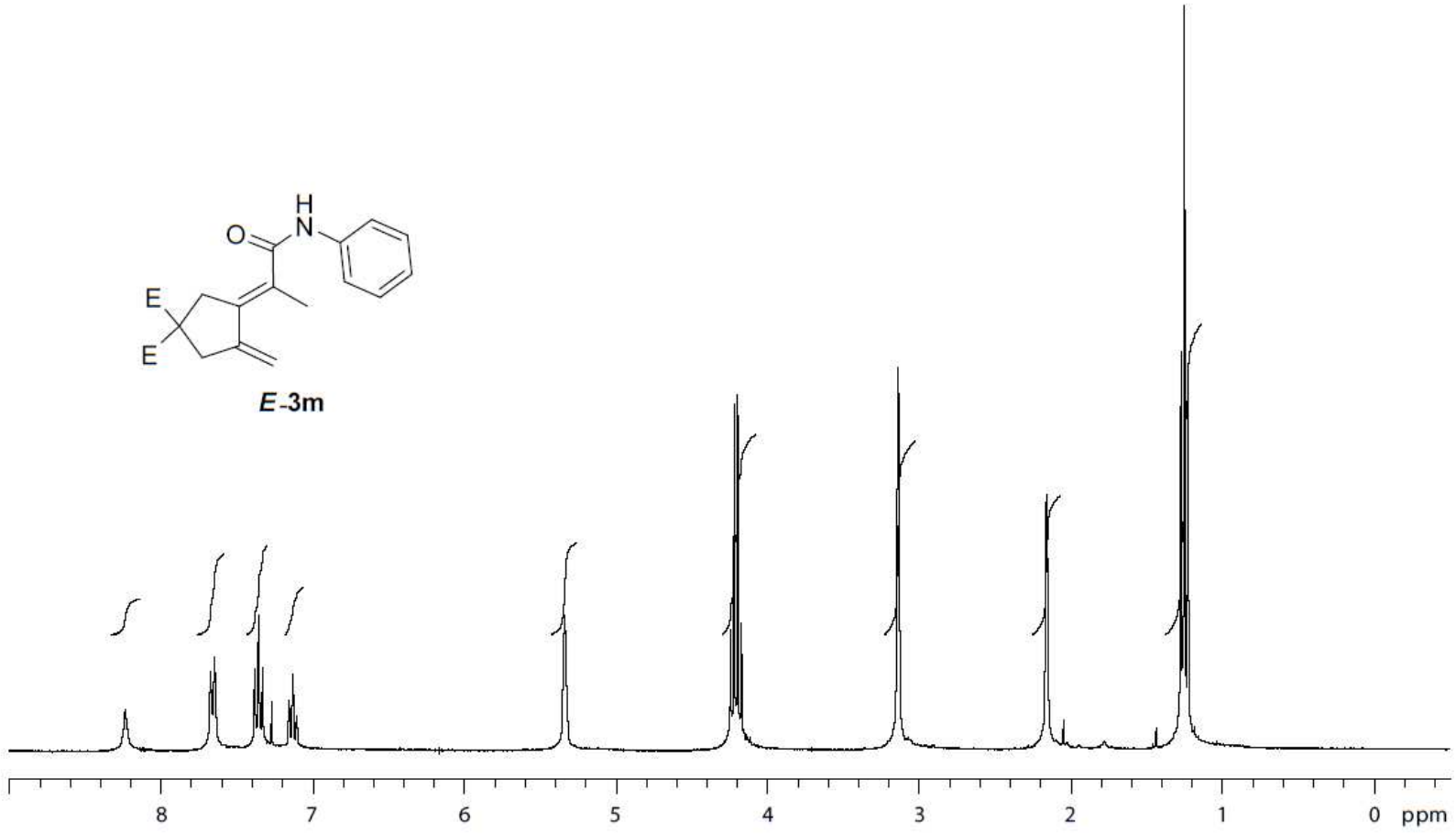
5.274
5.245
2.061
ppm
E-3l



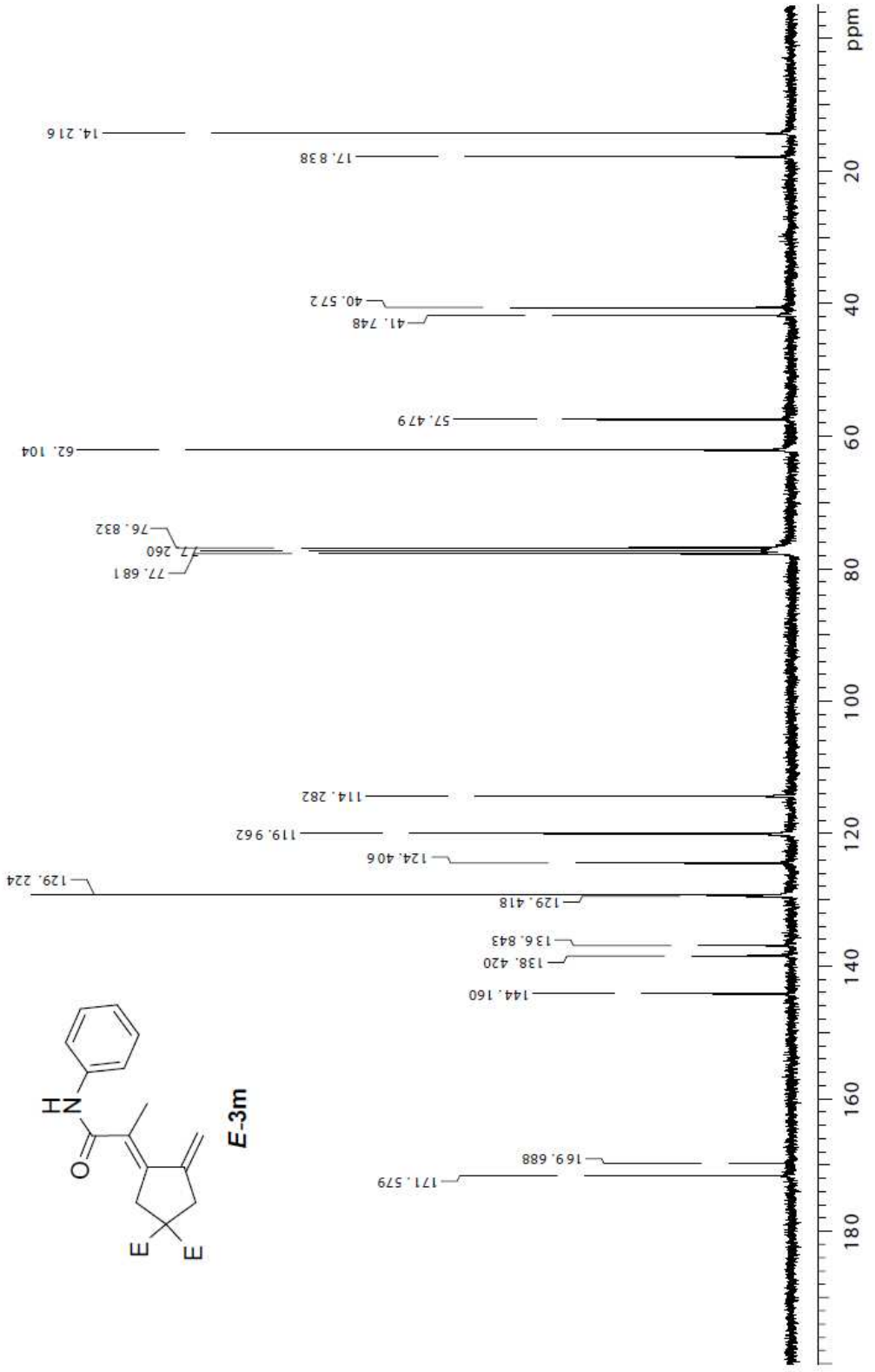
Z-3l

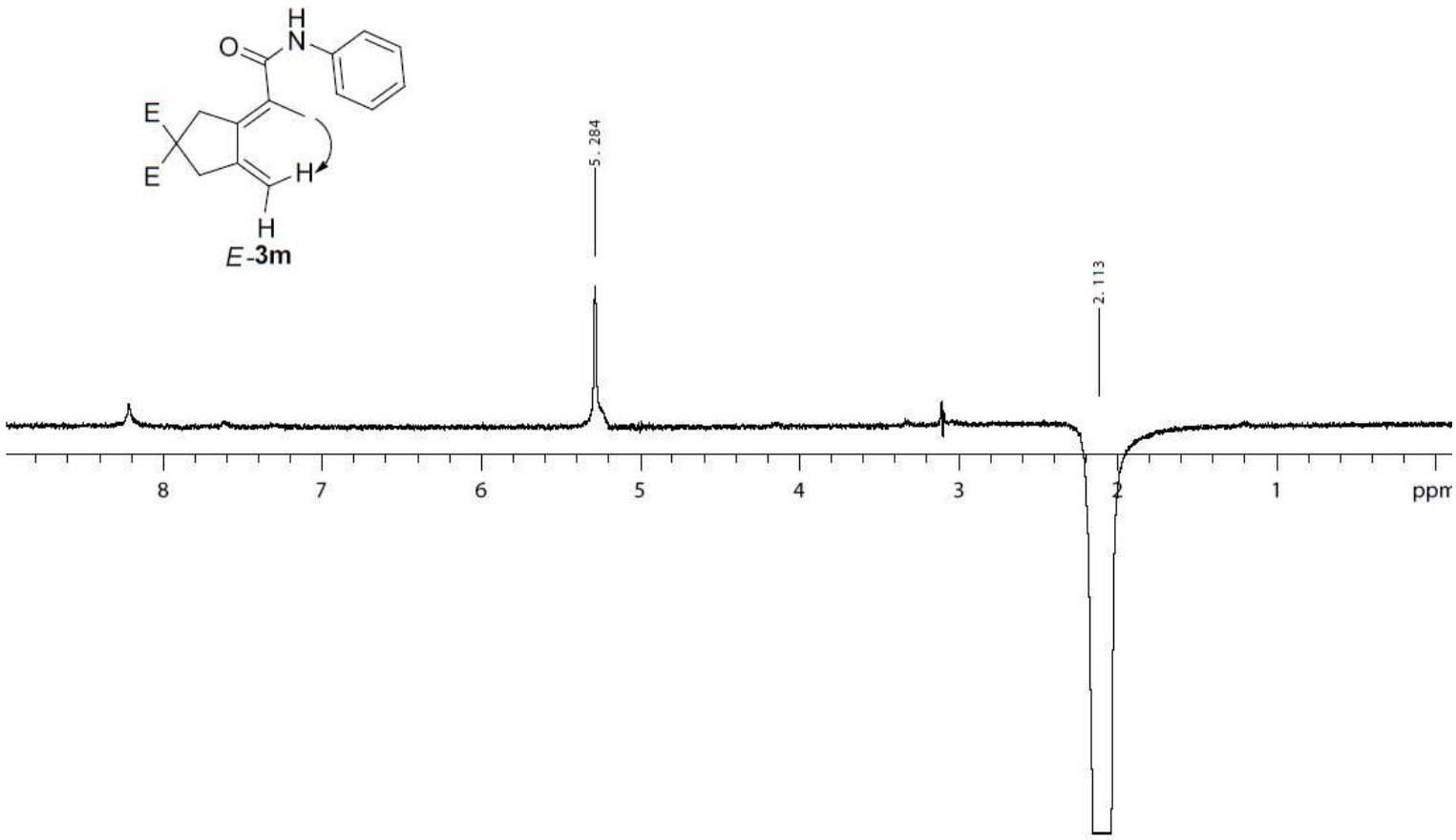
ppm
20
40
60
80
100
120
140
160
180
14.257
19.175
25.049
25.736
29.927
30.541
32.750
39.051
42.461
48.088
57.011
61.970
76.833
77.260
77.680
98.824
111.044
128.537
134.350
142.586
170.697
171.438
H
N
O
E
E
Z-3l

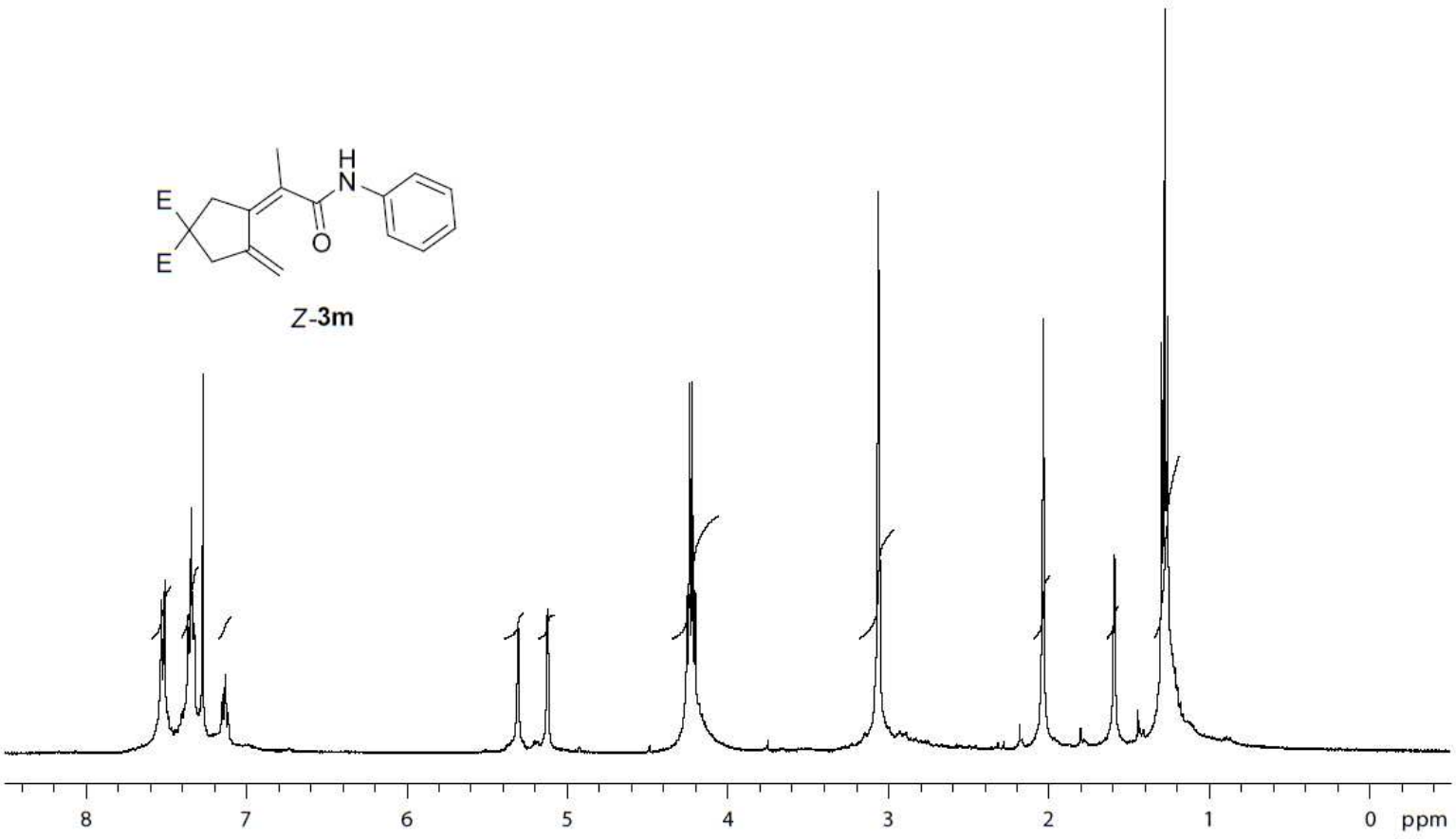
5.066
5.322
0
1
2
3
4
5
6
7
8
ppm
H
N
O
H
E
E
Z-3l

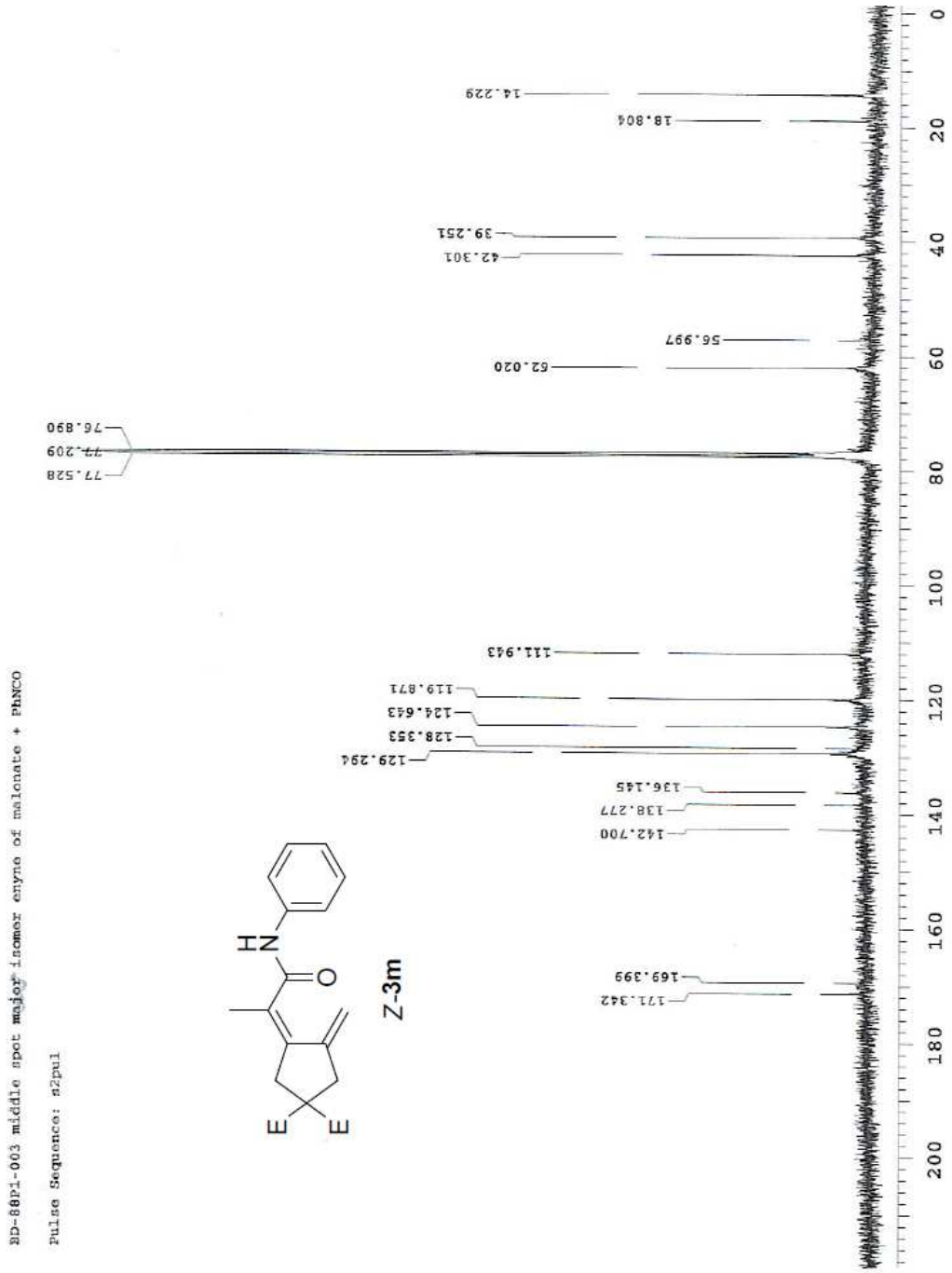


***E*-3m**


ppm
20
40
60
80
100
120
140
160
180
14.216
17.838
40.572
41.748
57.479
62.104
76.832
77.260
77.681
114.282
119.962
124.406
129.224
129.418
136.843
138.420
144.160
169.688
171.579
H
N
O
E
E
E-3m


O
H
N
E
E
H
H
E-3m
5.284
2.113
8
7
6
5
4
3
2
1
ppm

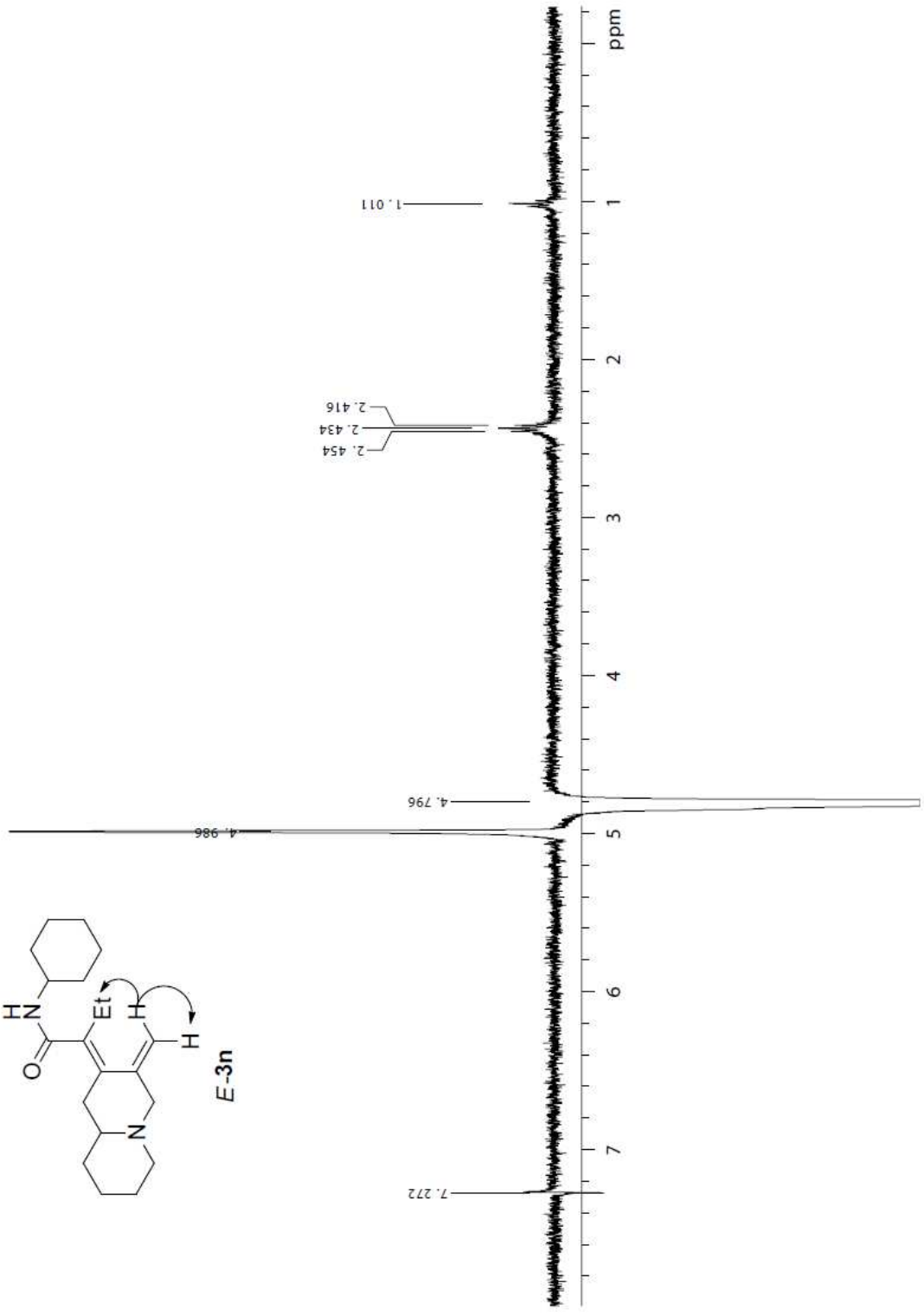

E
E
H
N
O
Z-3m
8
7
6
5
4
3
2
1
0
ppm

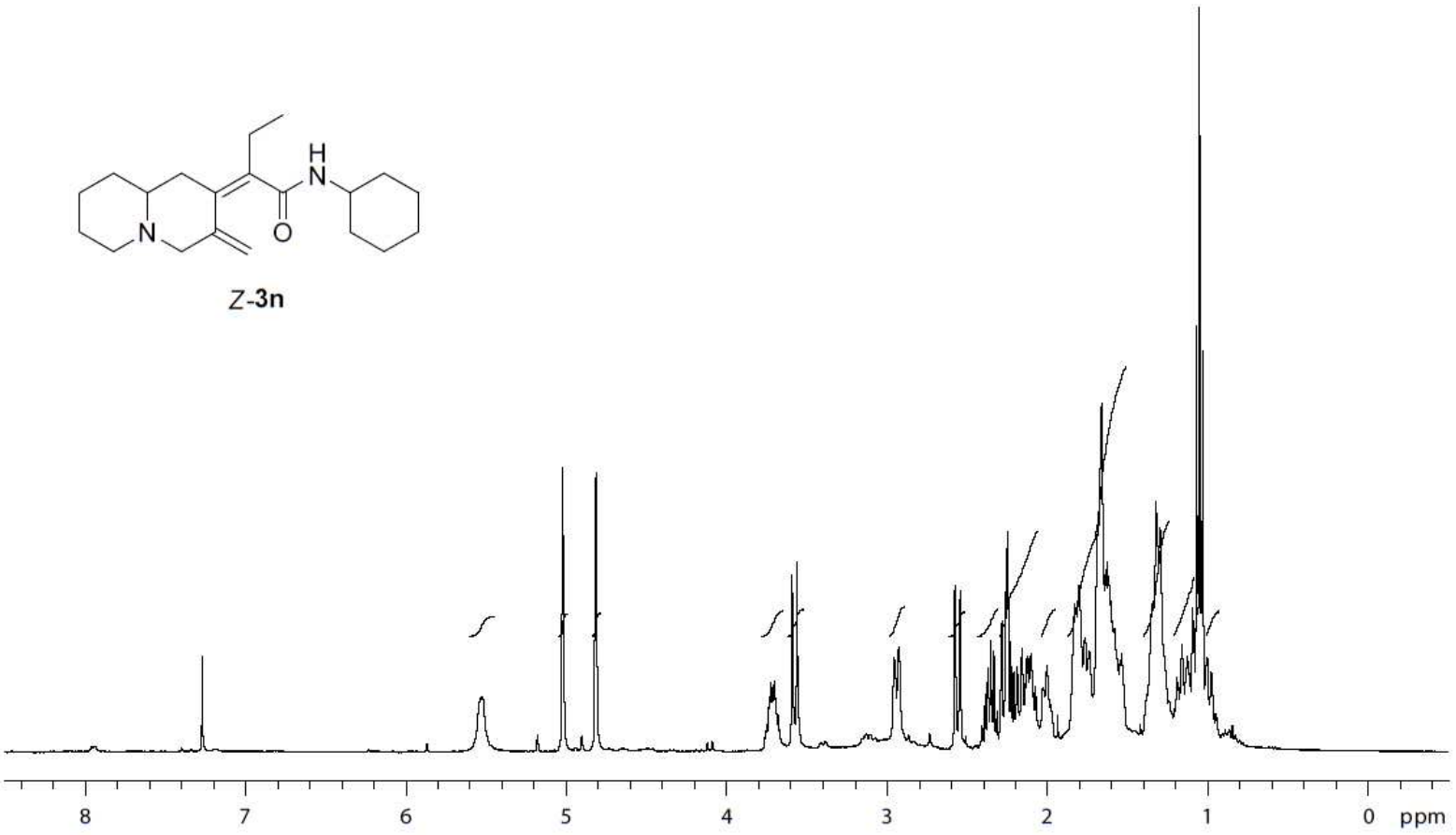

ED-88P1-003 middle spot major isomer enyne of malonate + PhNCO
Pulse Sequence: s2pul
Z-3m
14.229
18.804
39.251
42.301
56.997
62.020
76.890
77.209
77.528
111.943
119.871
124.643
128.353
129.294
136.145
138.277
142.700
169.399
171.342
0
20
40
60
80
100
120
140
160
180
200

5.306
5.123
3.060
0 ppm
Z-3m

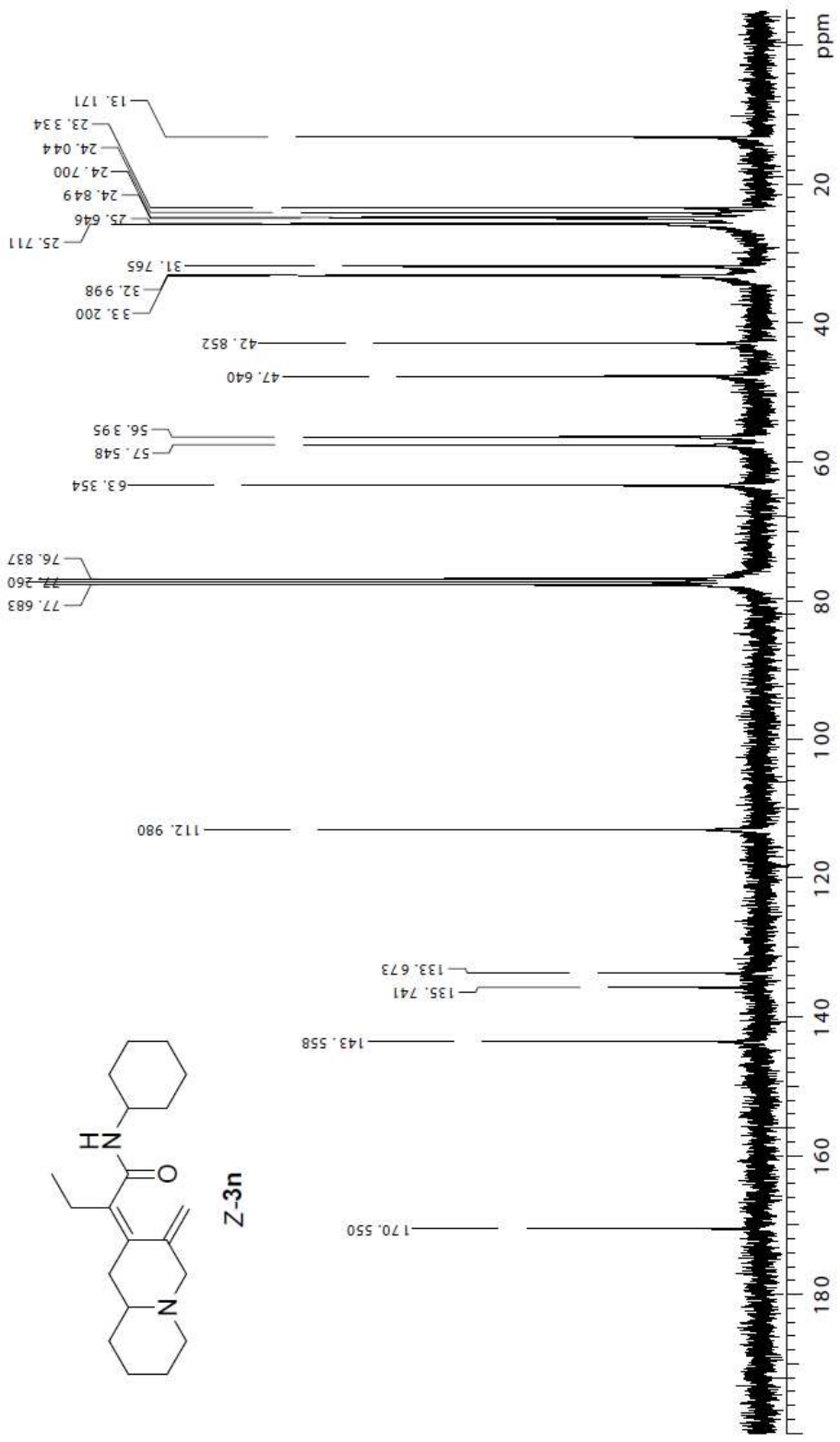
H
N
O
Et
N
E-3n
8
7
6
5
4
3
2
1
0
ppm

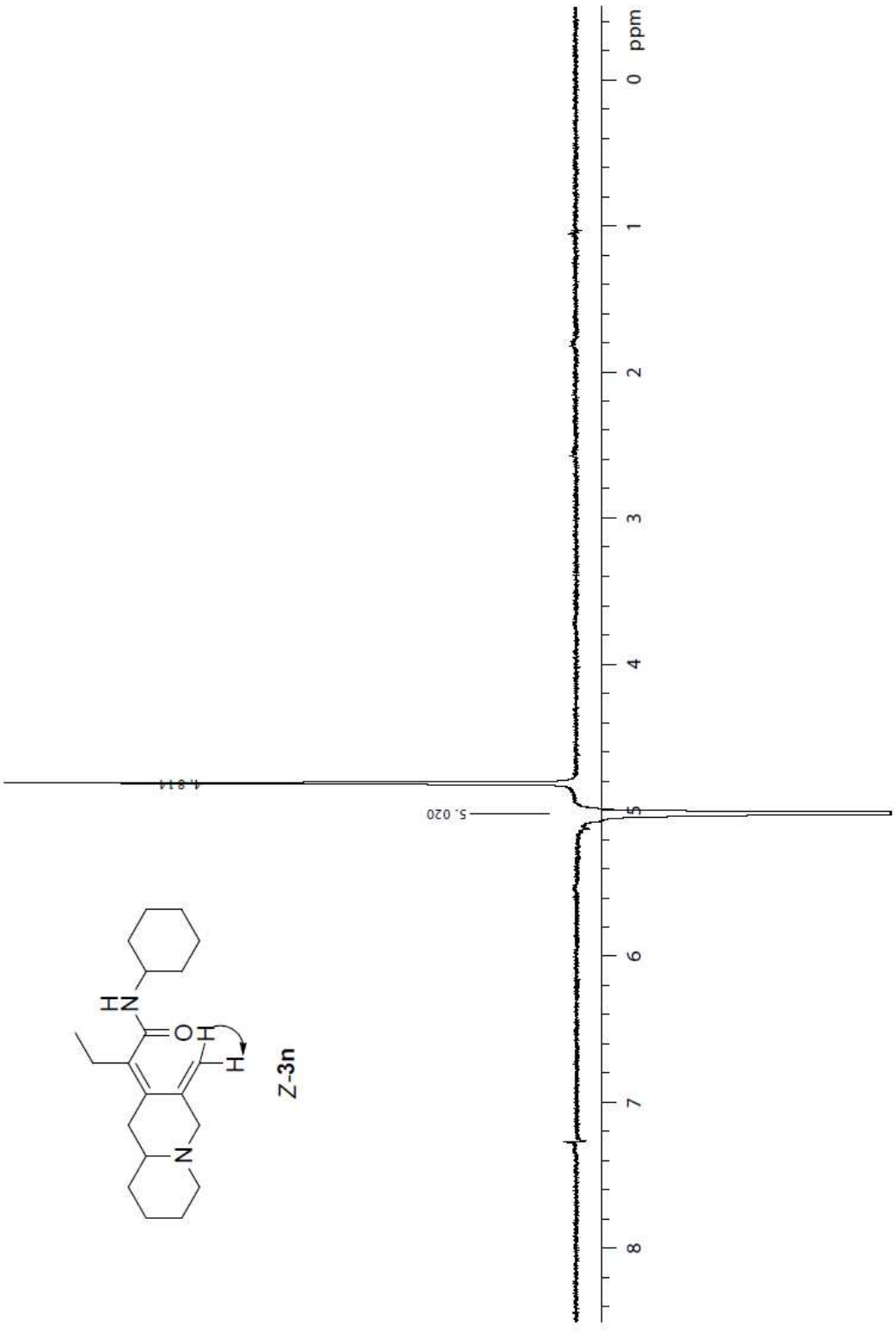
169.873
143.873
134.687
134.401
111.922
110.232
77.693
77.270
76.847
63.974
60.636
56.173
48.359
43.682
33.488
32.969
25.828
25.767
25.240
24.153
23.977
13.604
ppm
E-3n


ppm
1
2
3
4
5
6
7
1.011
2.416
2.434
2.454
4.796
4.986
7.272
Et
H
H
N
O
N
E-3n

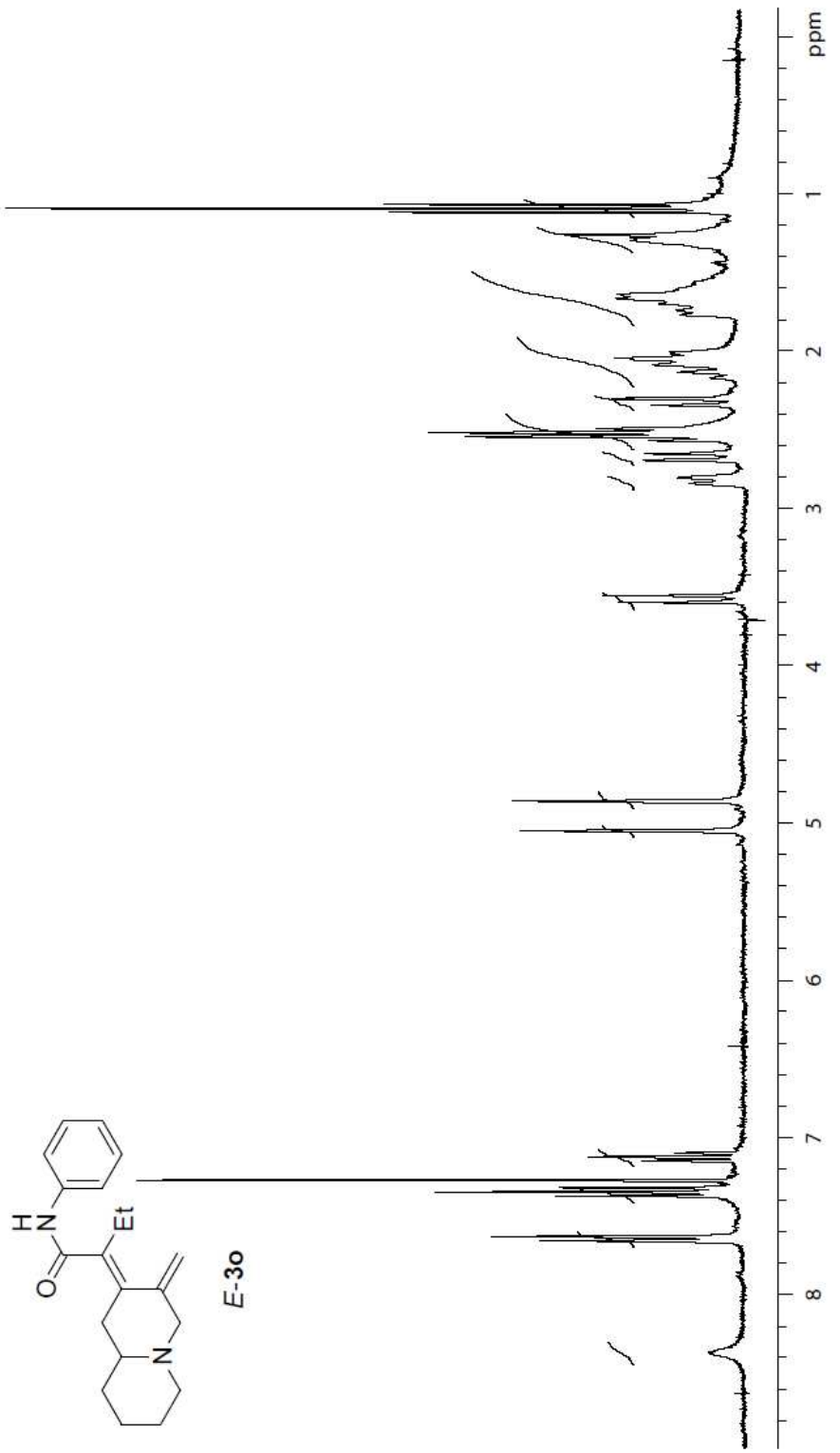


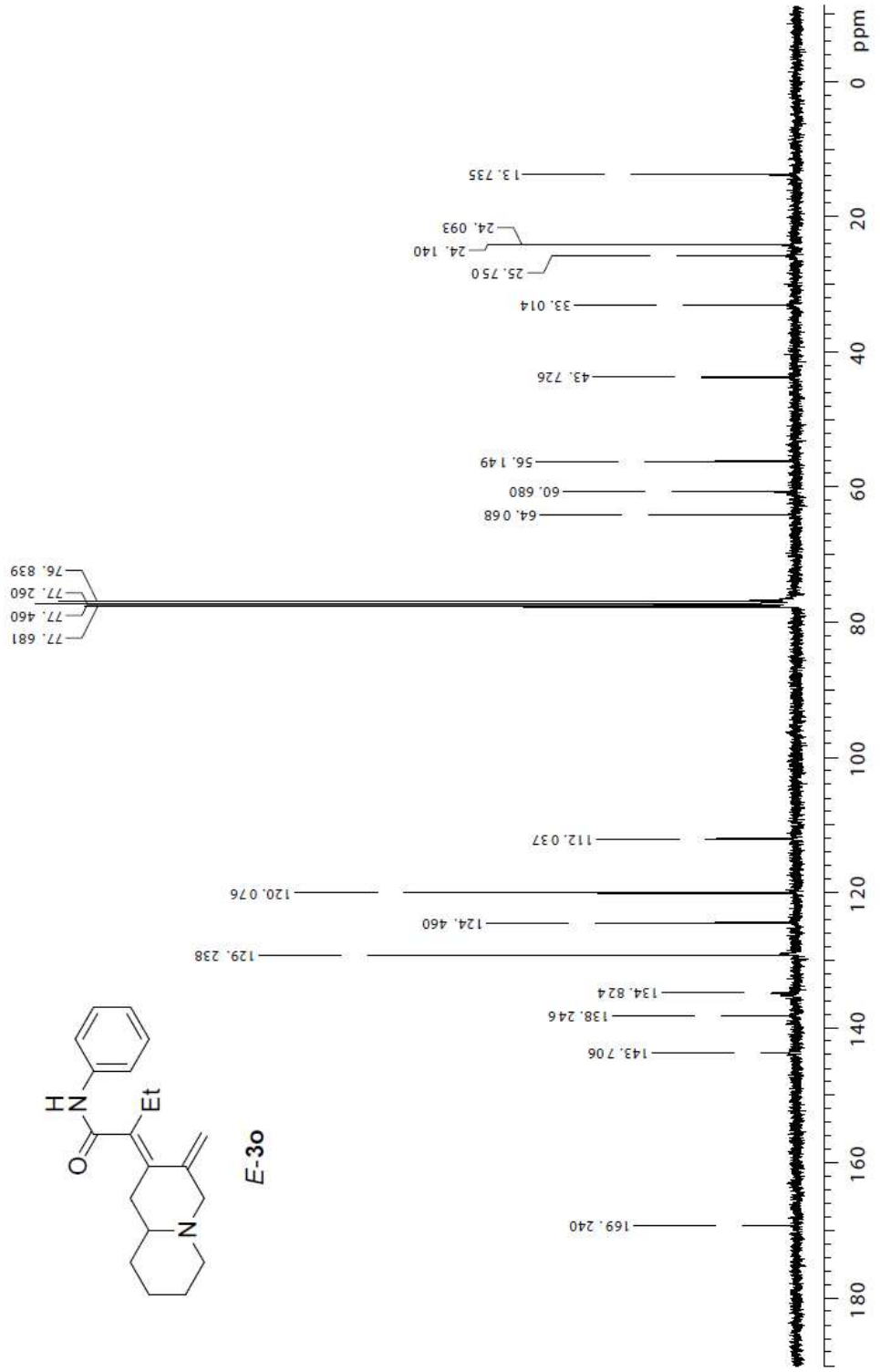
Z-**3n**

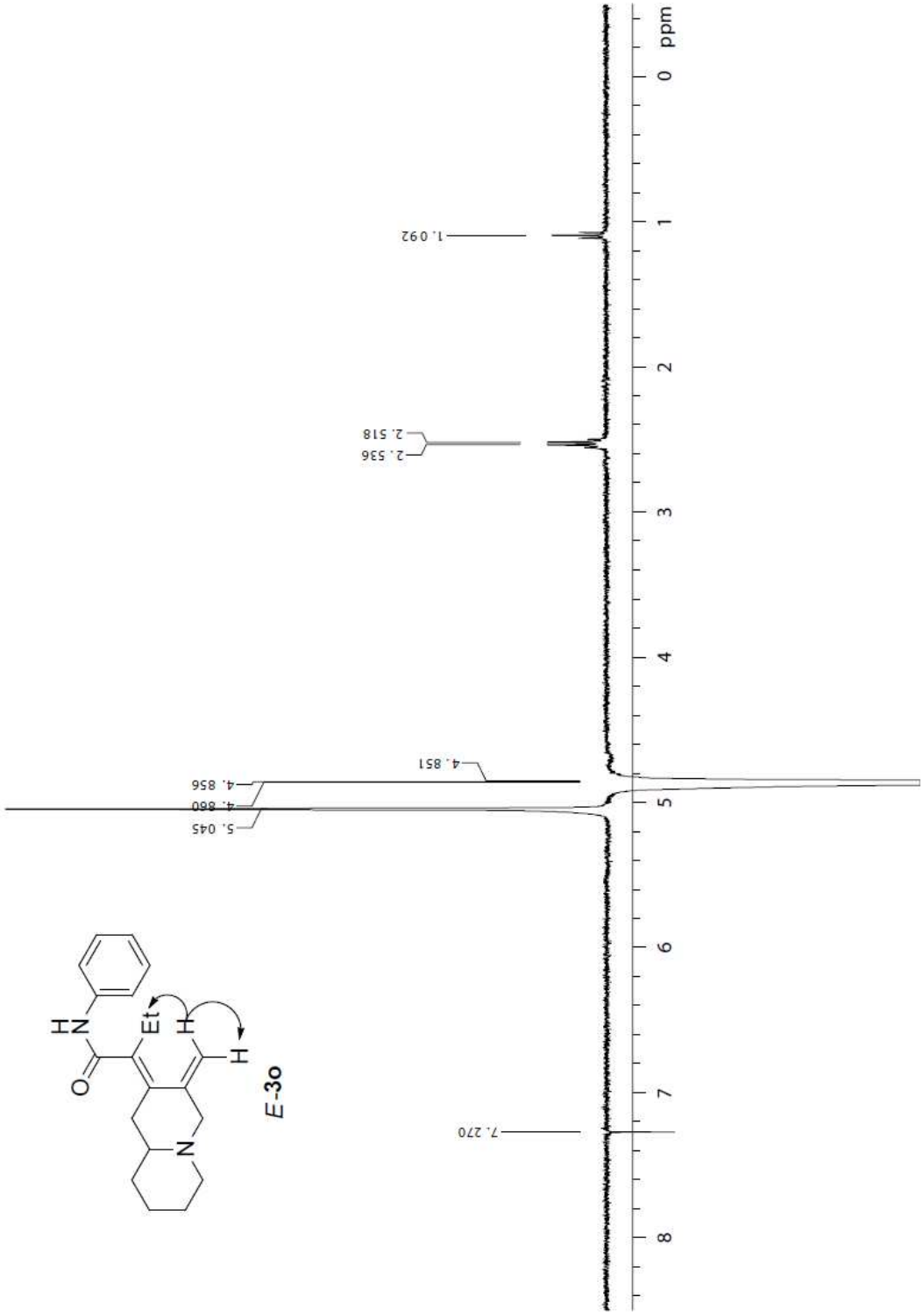

13.171
23.334
24.044
24.700
24.849
25.646
25.711
31.765
32.998
33.200
42.852
47.640
56.395
57.548
63.354
76.837
77.260
77.683
112.980
133.673
135.741
143.558
170.550
ppm
20
40
60
80
100
120
140
160
180
HN
O
N
Z-3n

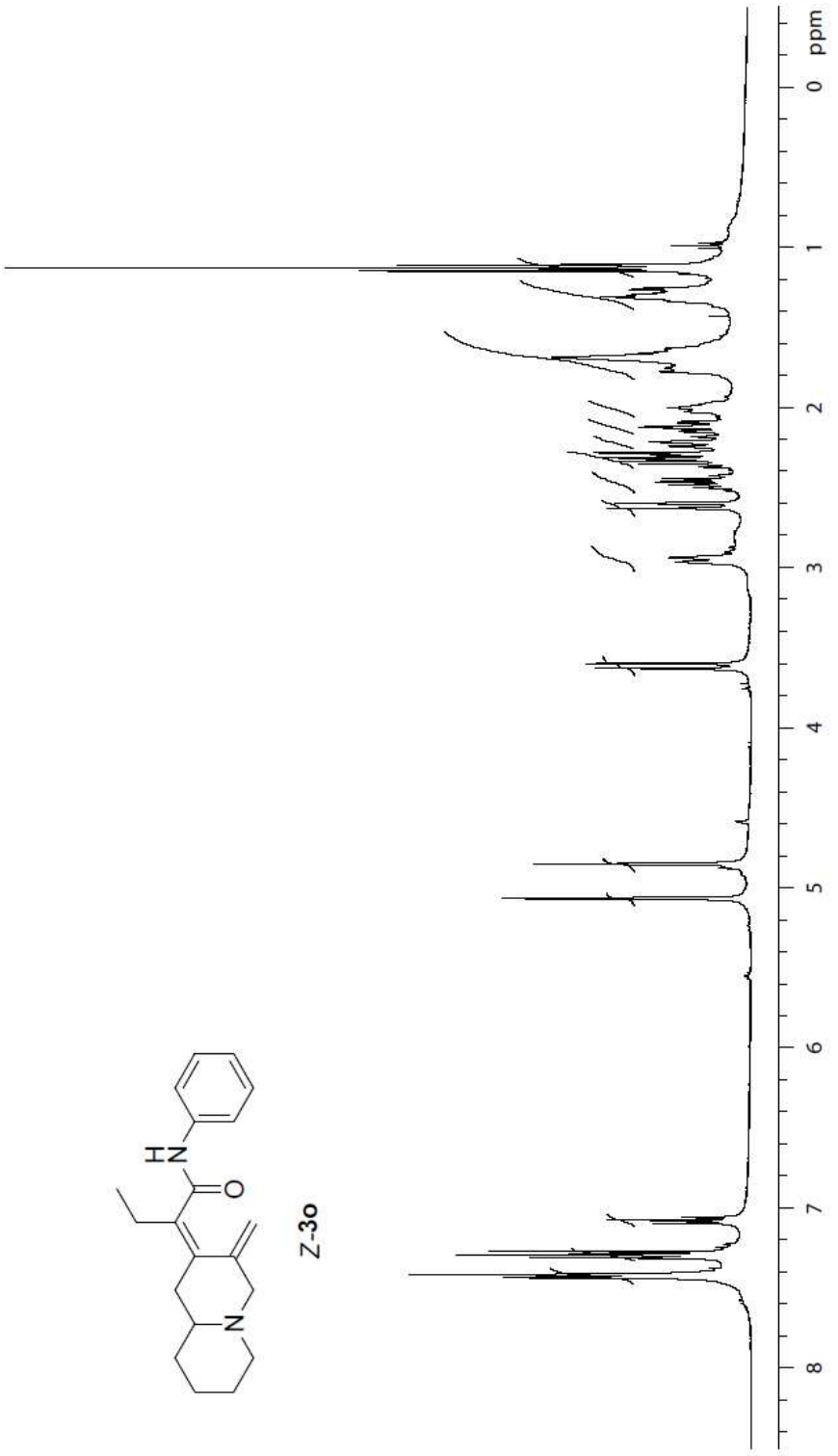


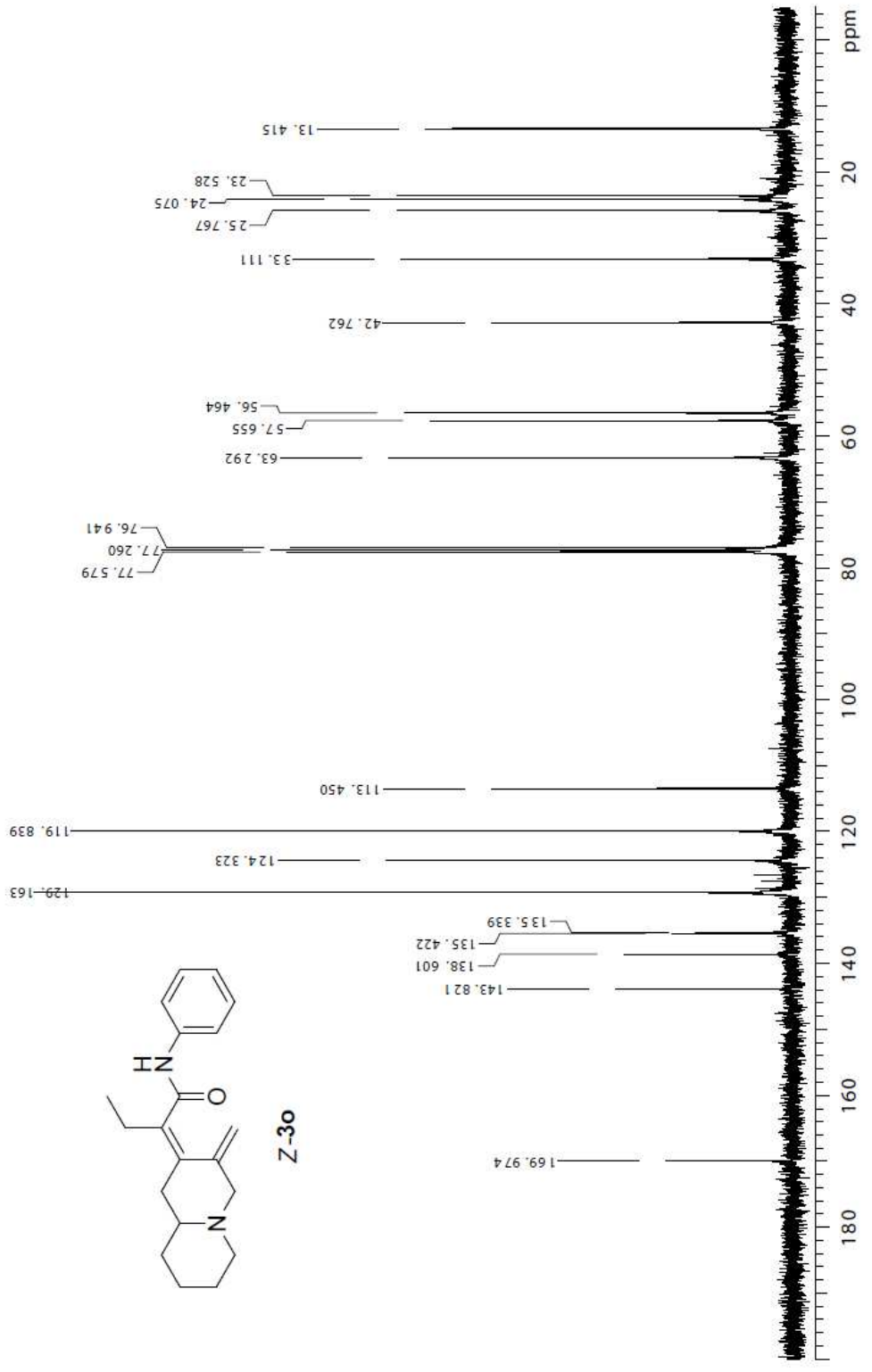
Z-3n

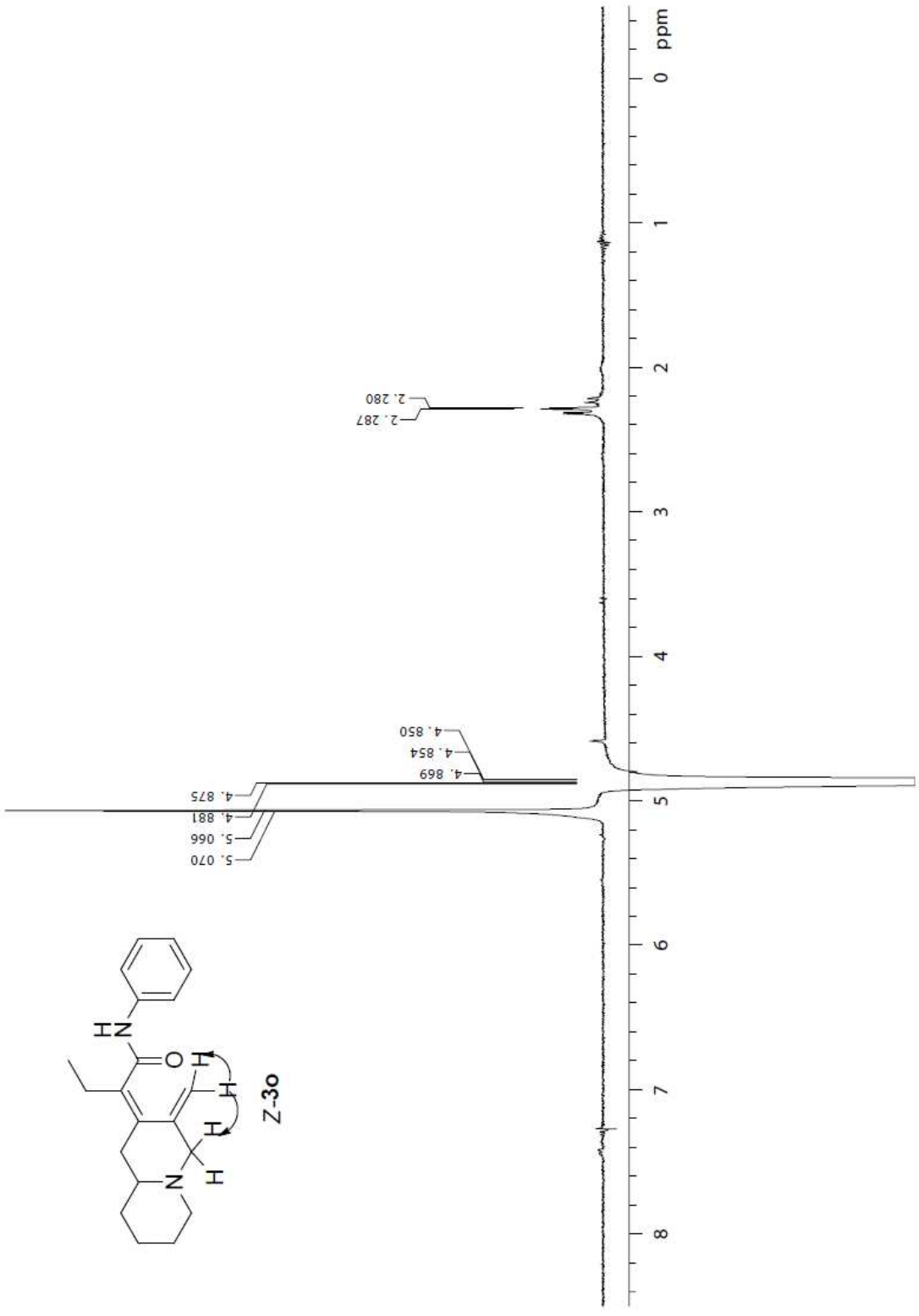

H
N
O
Et
N
E-3o
ppm
1
2
3
4
5
6
7
8

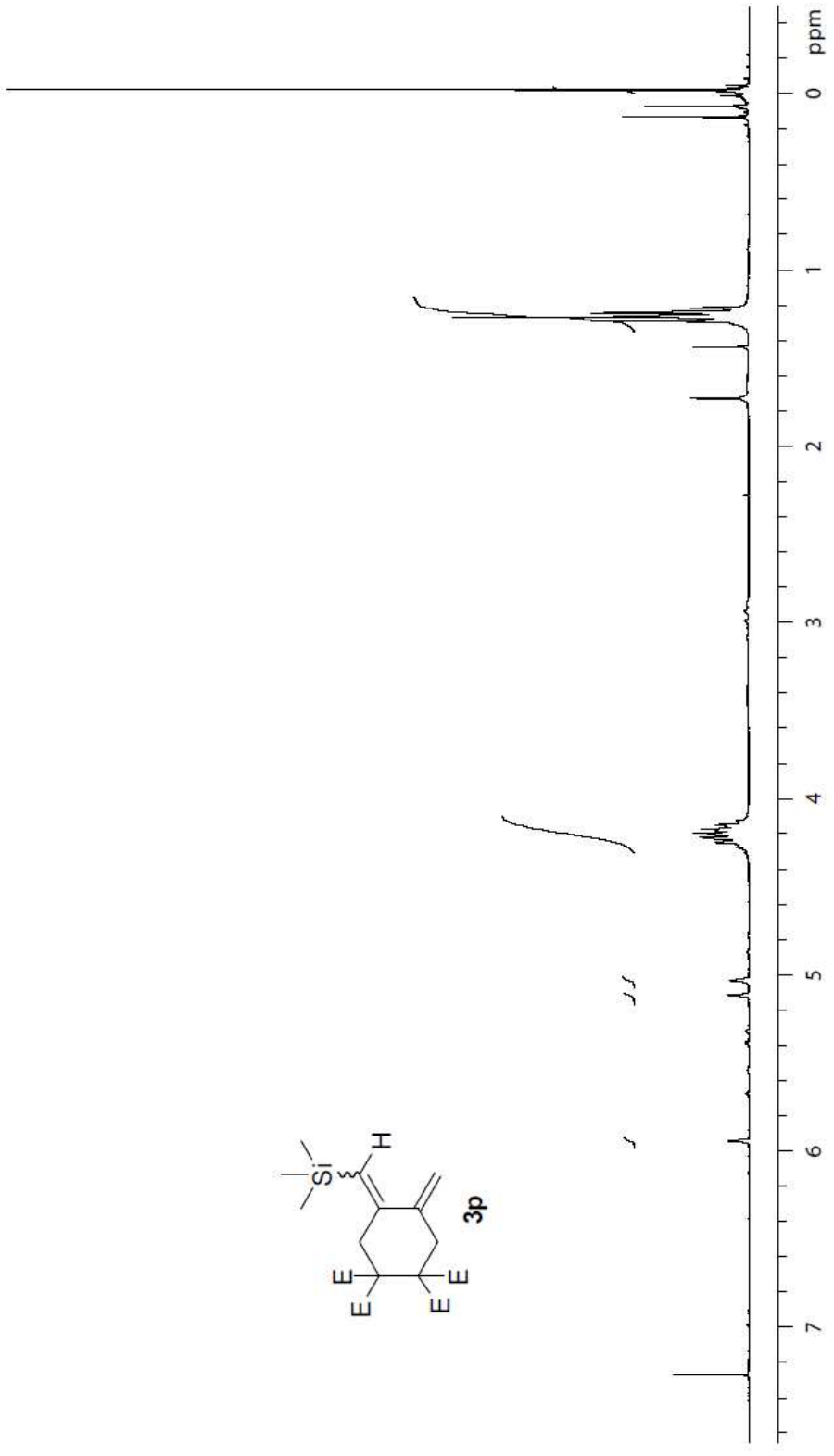

13.735
24.093
24.140
25.750
33.014
43.726
56.149
60.680
64.068
76.839
77.260
77.460
77.681
112.037
120.076
124.460
129.238
134.824
138.246
143.706
169.240
0
20
40
60
80
100
120
140
160
180
ppm
H
N
O
Et
N
E-3o

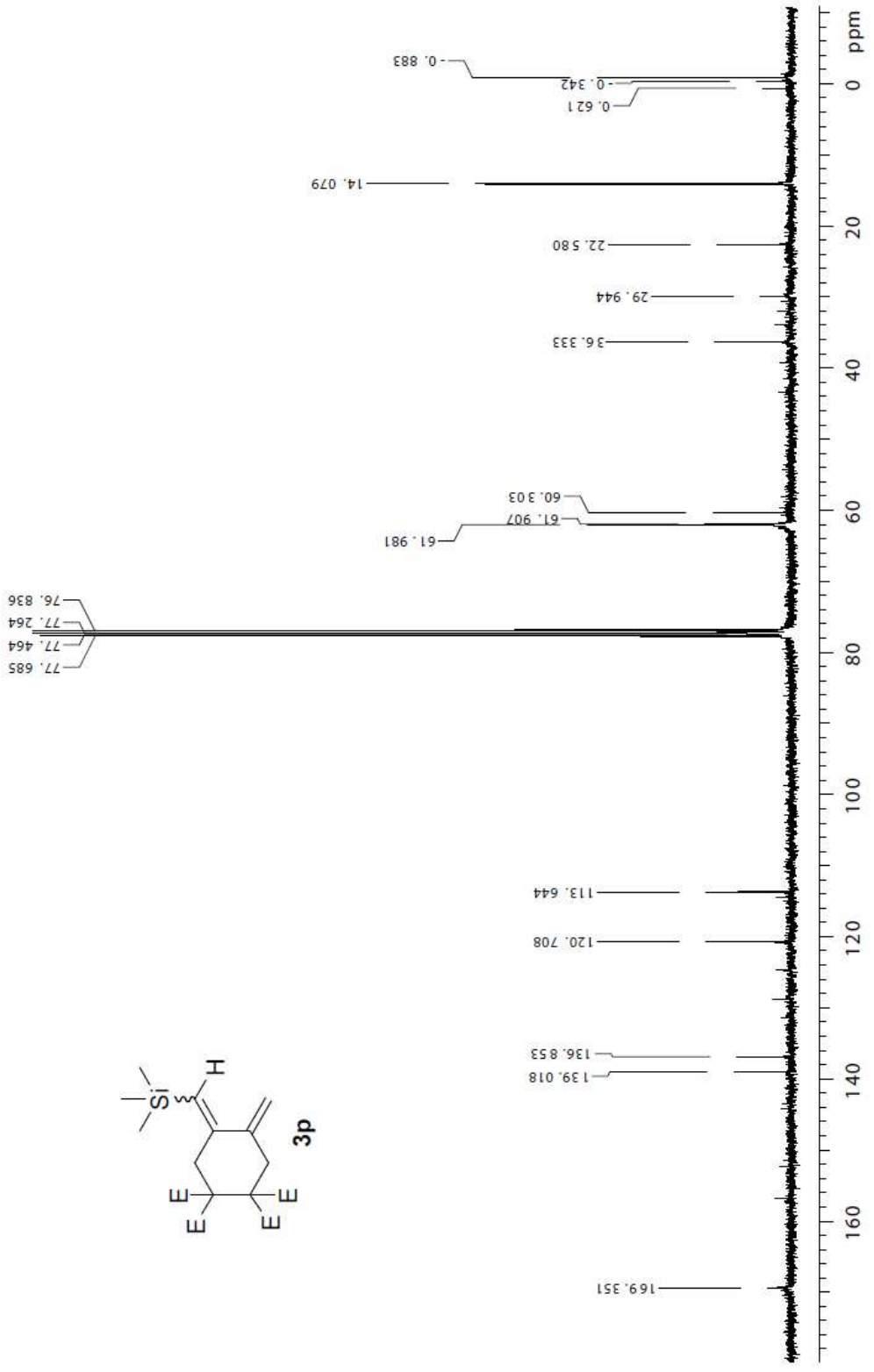

ppm
0
1
2
3
4
5
6
7
8
1.092
2.536
2.518
4.851
4.856
4.860
5.045
7.270
H
N
O
Et
H
H
N
E-3o

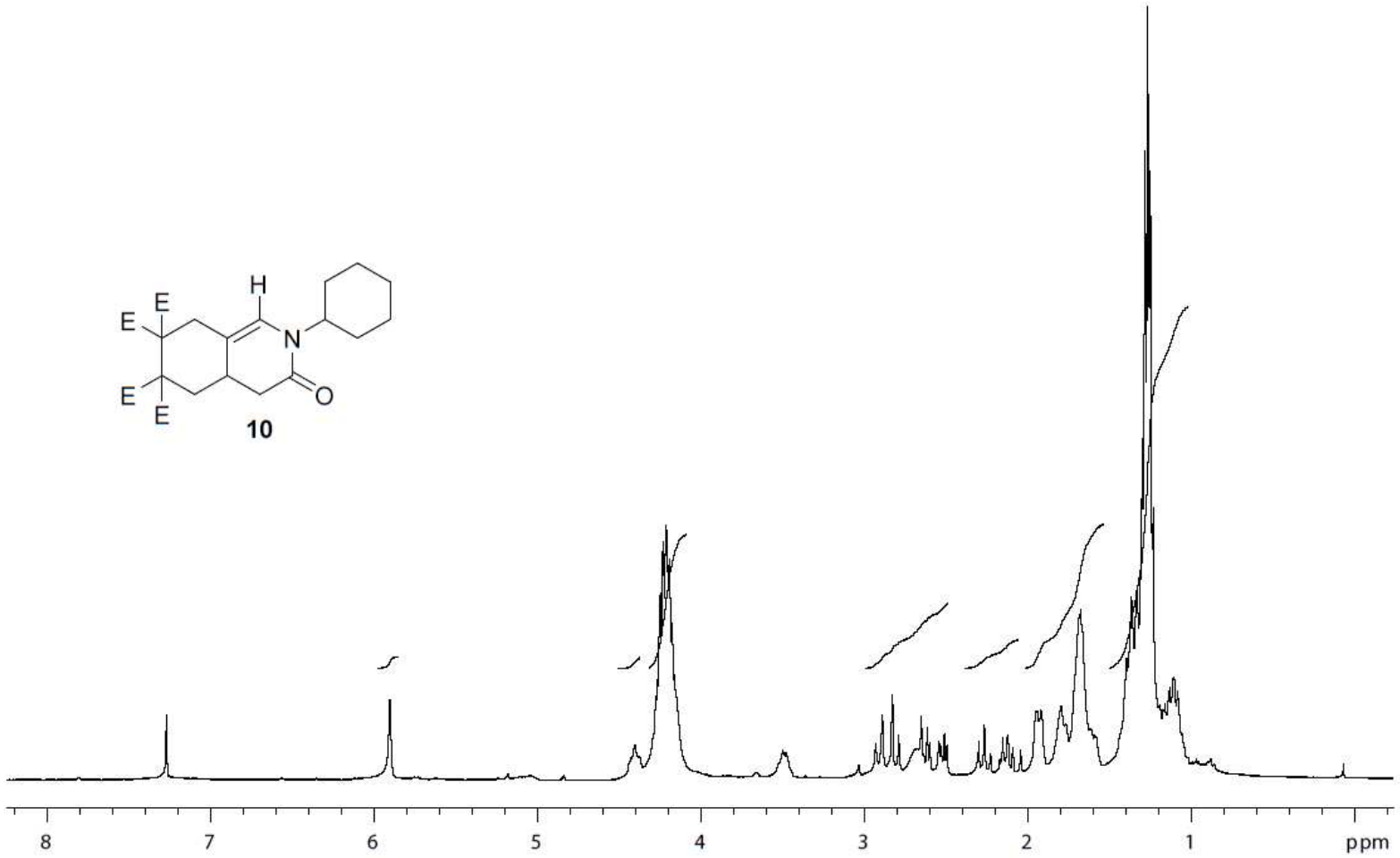

H
N
O
N
Z-3o
8
7
6
5
4
3
2
1
0 ppm

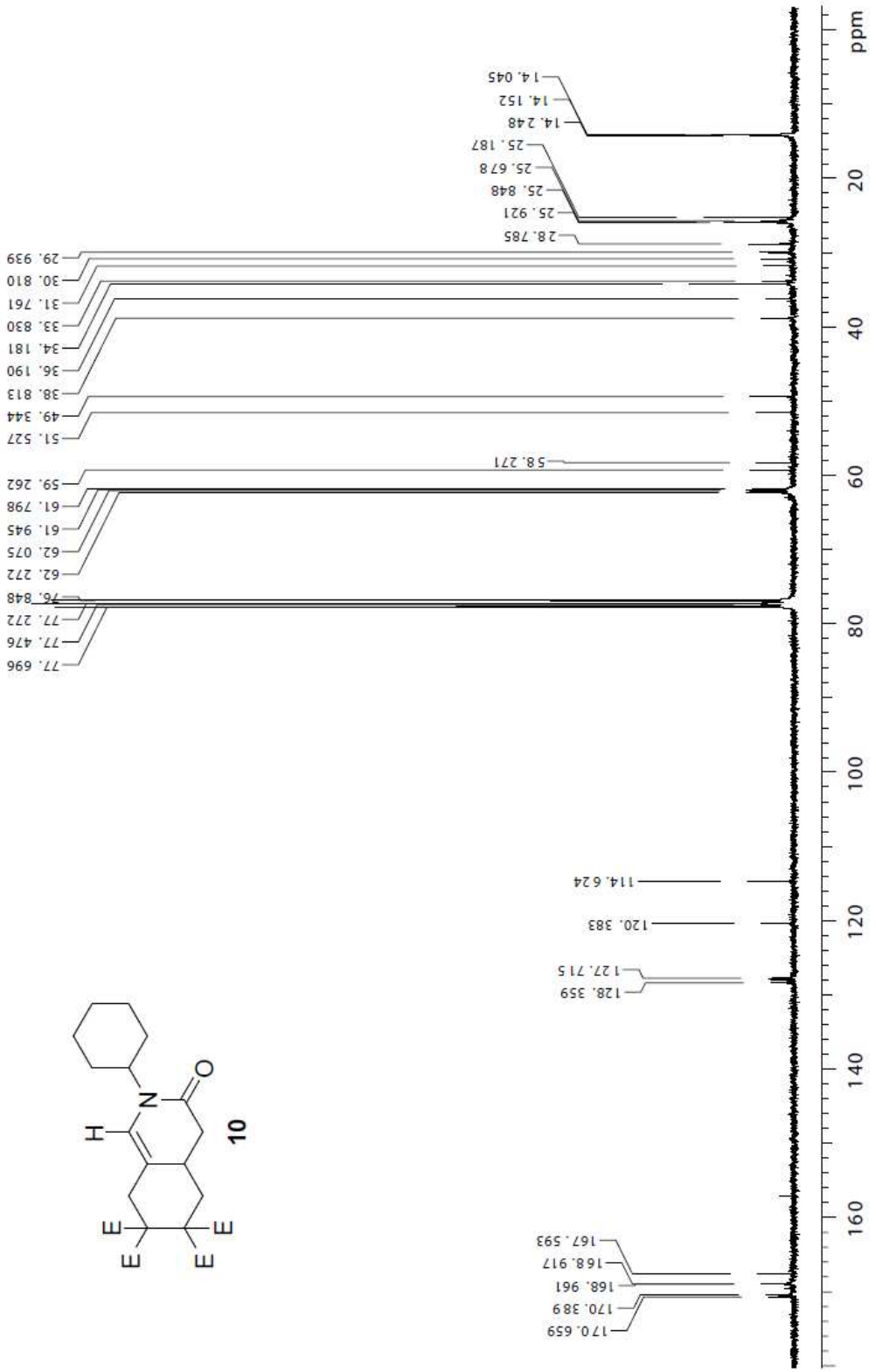

ppm
20
40
60
80
100
120
140
160
180
13.415
23.528
24.075
25.767
33.111
42.762
56.464
57.655
63.292
76.941
77.260
77.579
113.450
119.839
124.323
129.163
135.339
135.422
138.601
143.821
169.974
HN
O
N
Z-3o

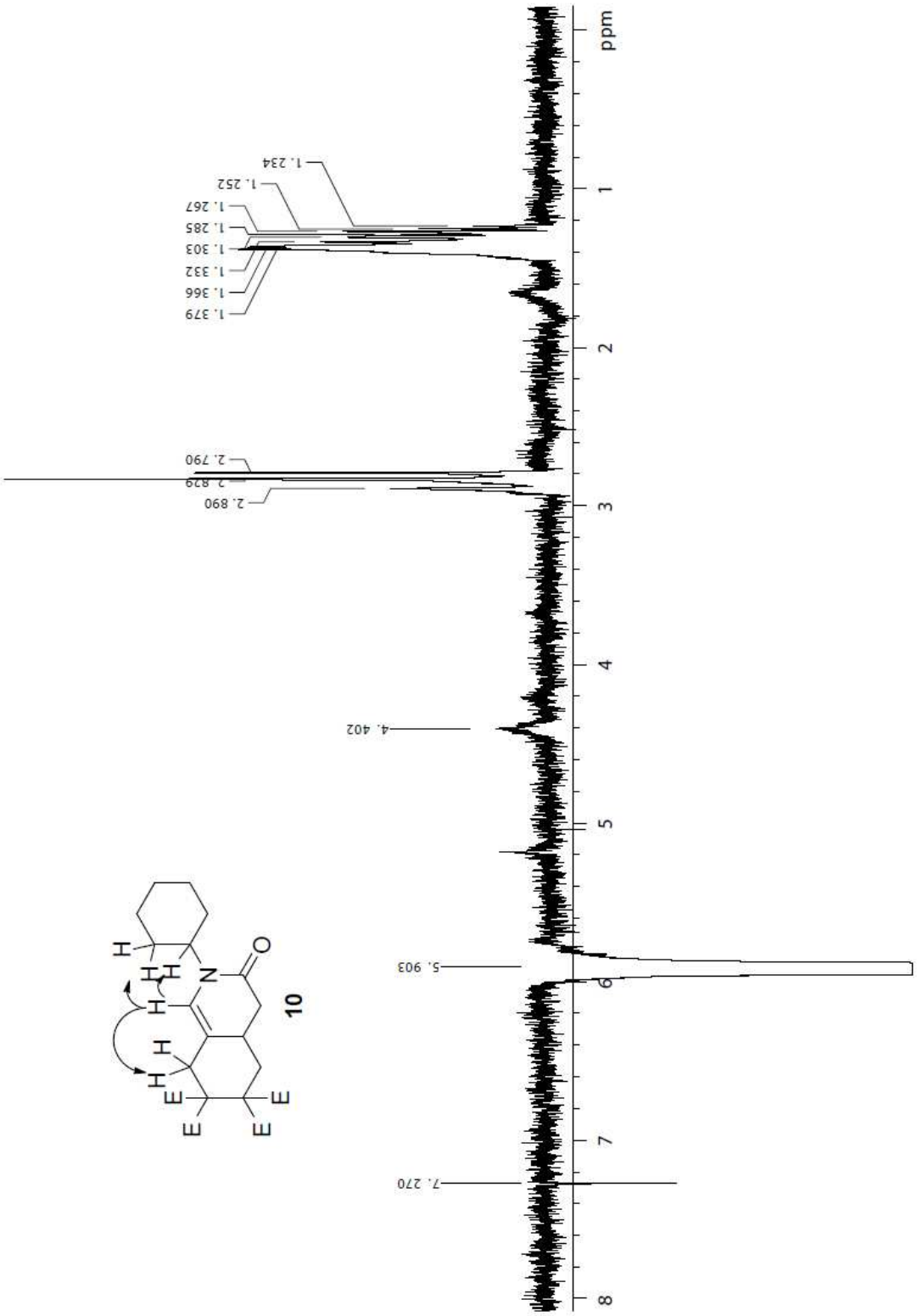

2.287
2.280
4.869
4.854
4.850
5.070
5.066
4.881
4.875
ppm
0
1
2
3
4
5
6
7
8
Z-3o

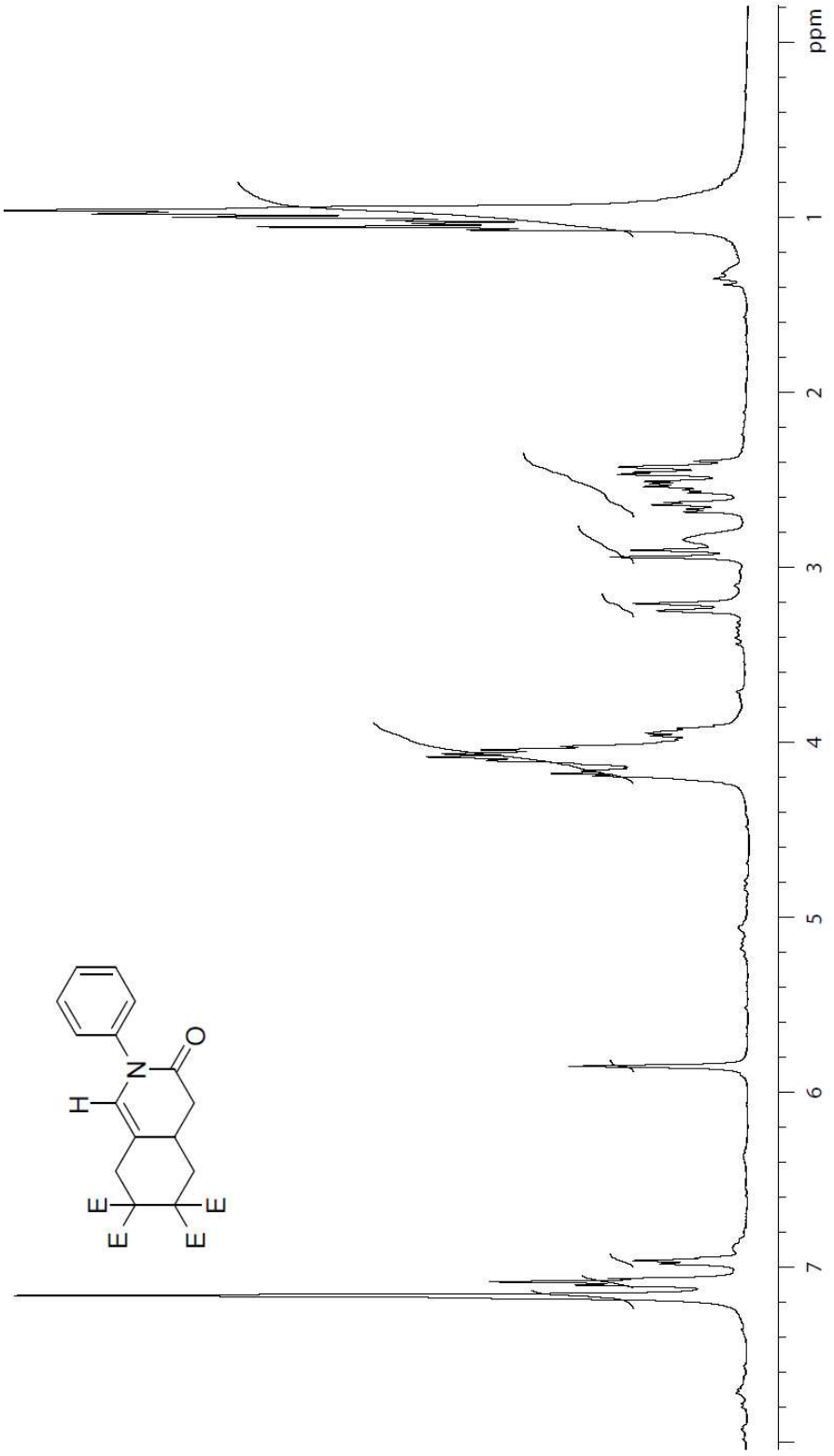

Si
H
E
E
E
E
3p
ppm
0
1
2
3
4
5
6
7

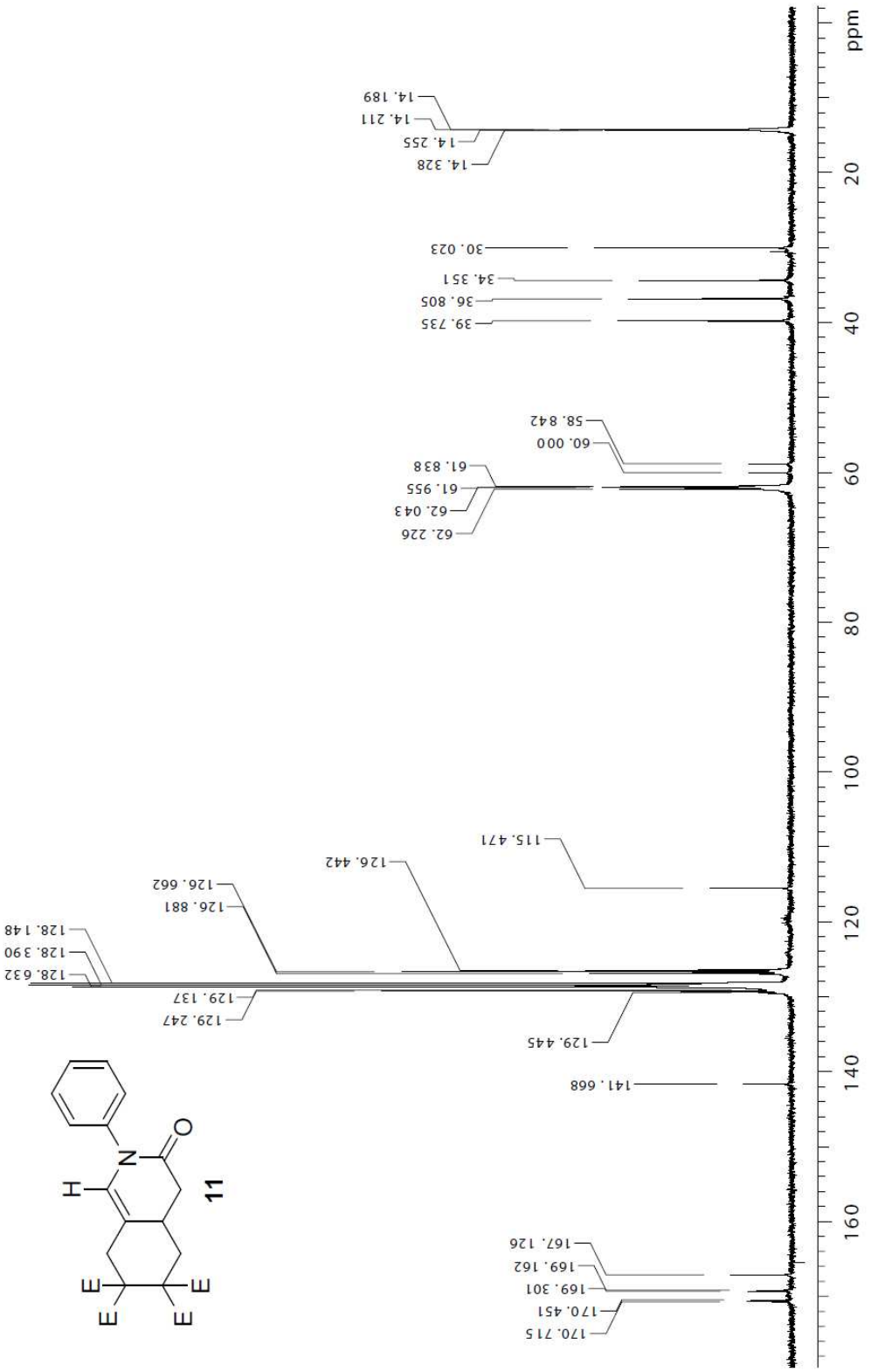

ppm
0
20
40
60
80
100
120
140
160
-0.883
0.342
0.621
14.079
22.580
29.944
36.333
60.303
61.907
61.981
76.836
77.264
77.464
77.685
113.644
120.708
136.853
139.018
169.351
Si
E
E
E
E
3p


H
E
E
E
E
N
O
10
8
7
6
5
4
3
2
1
ppm

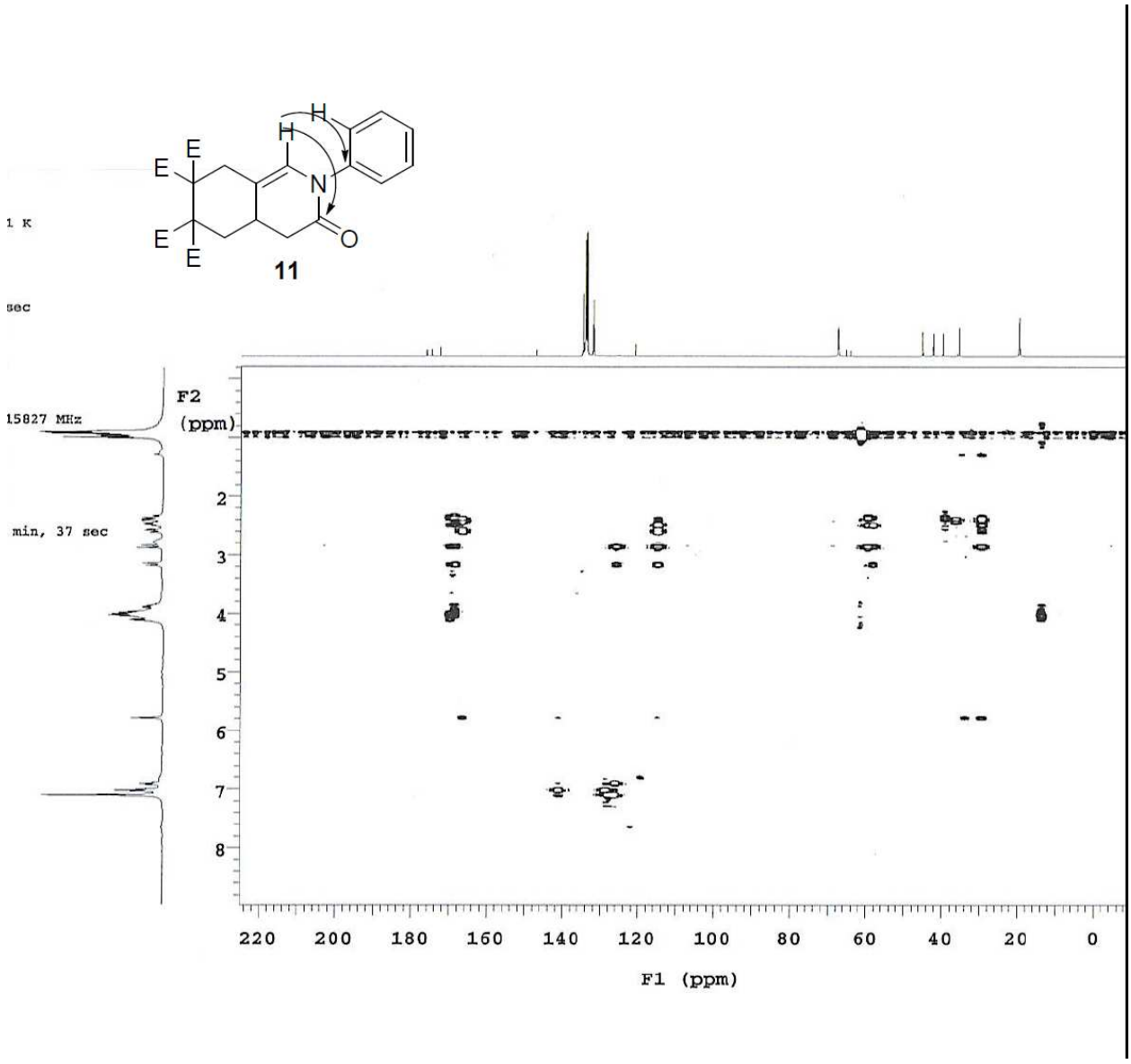

ppm
20
40
60
80
100
120
140
160
14.045
14.152
14.248
25.187
25.678
25.848
25.921
28.785
29.939
30.810
31.761
33.830
34.181
36.190
38.813
49.344
51.527
58.271
59.262
61.798
61.945
62.075
62.272
76.848
77.272
77.476
77.696
114.624
120.383
127.715
128.359
167.593
168.917
168.961
170.389
170.659
O
N
H
E
E
E
E
10

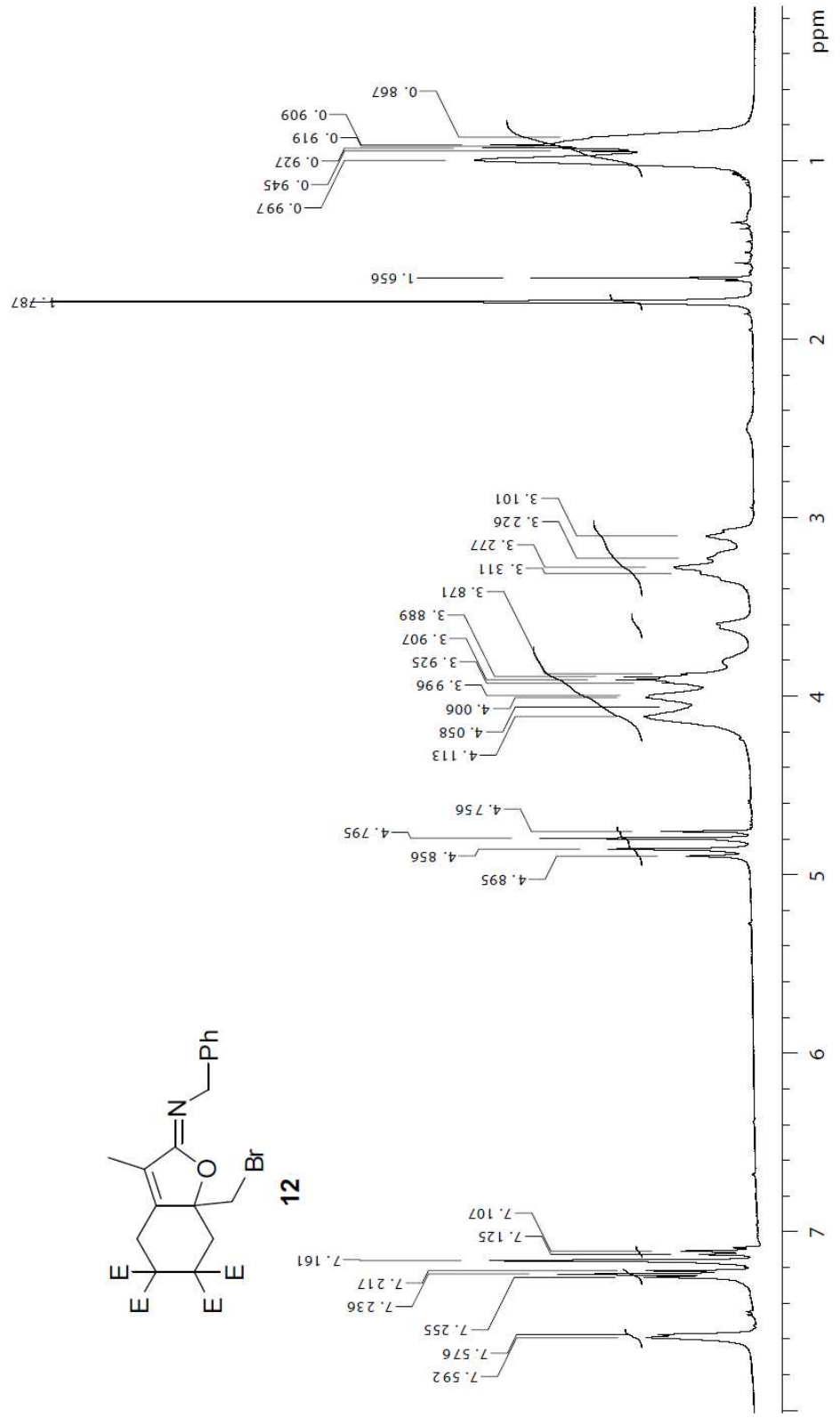

ppm
1
2
3
4
5
6
7
8
1.234
1.252
1.267
1.285
1.303
1.332
1.366
1.379
2.790
2.829
2.890
4.402
5.903
7.270
10

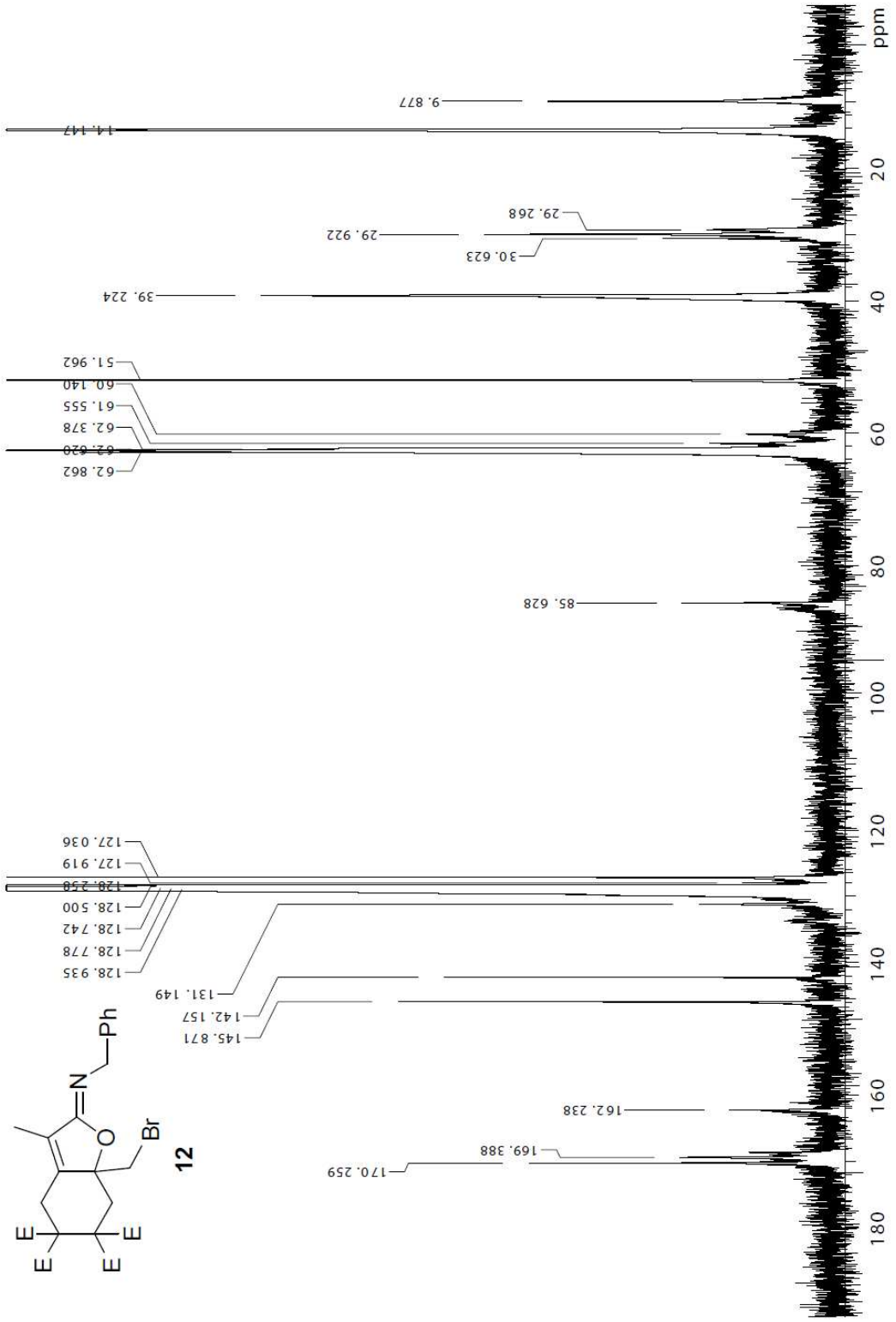

O
N
H
E
E
E
E
ppm
1
2
3
4
5
6
7

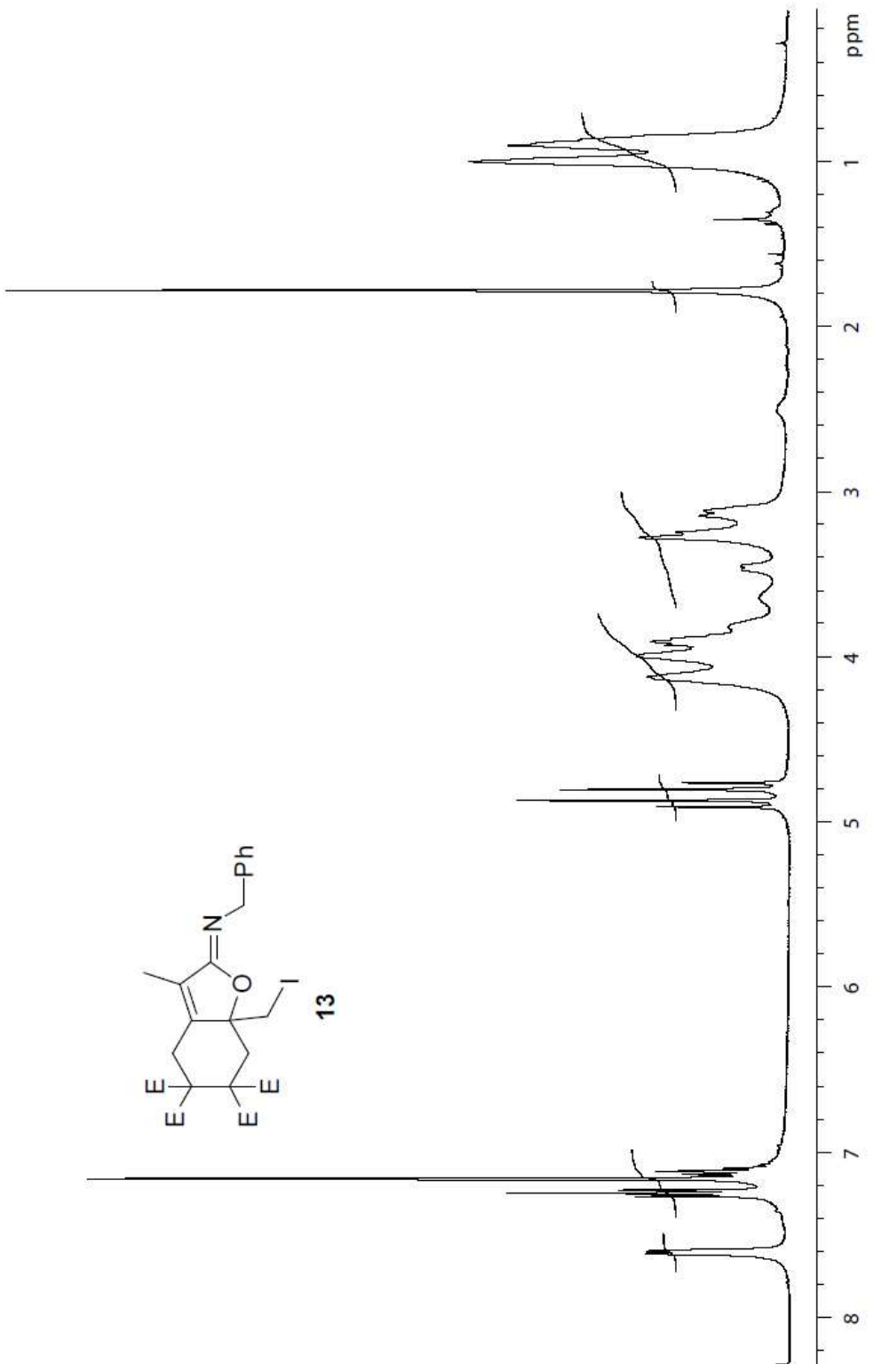

ppm
20
40
60
80
100
120
140
160
14.189
14.211
14.255
14.328
30.023
34.351
36.805
39.735
58.842
60.000
61.838
61.955
62.043
62.226
115.471
126.442
126.662
126.881
128.148
128.390
128.632
129.137
129.247
129.445
141.668
167.126
169.162
169.301
170.451
170.715
H
N
O
E
E
E
E
11

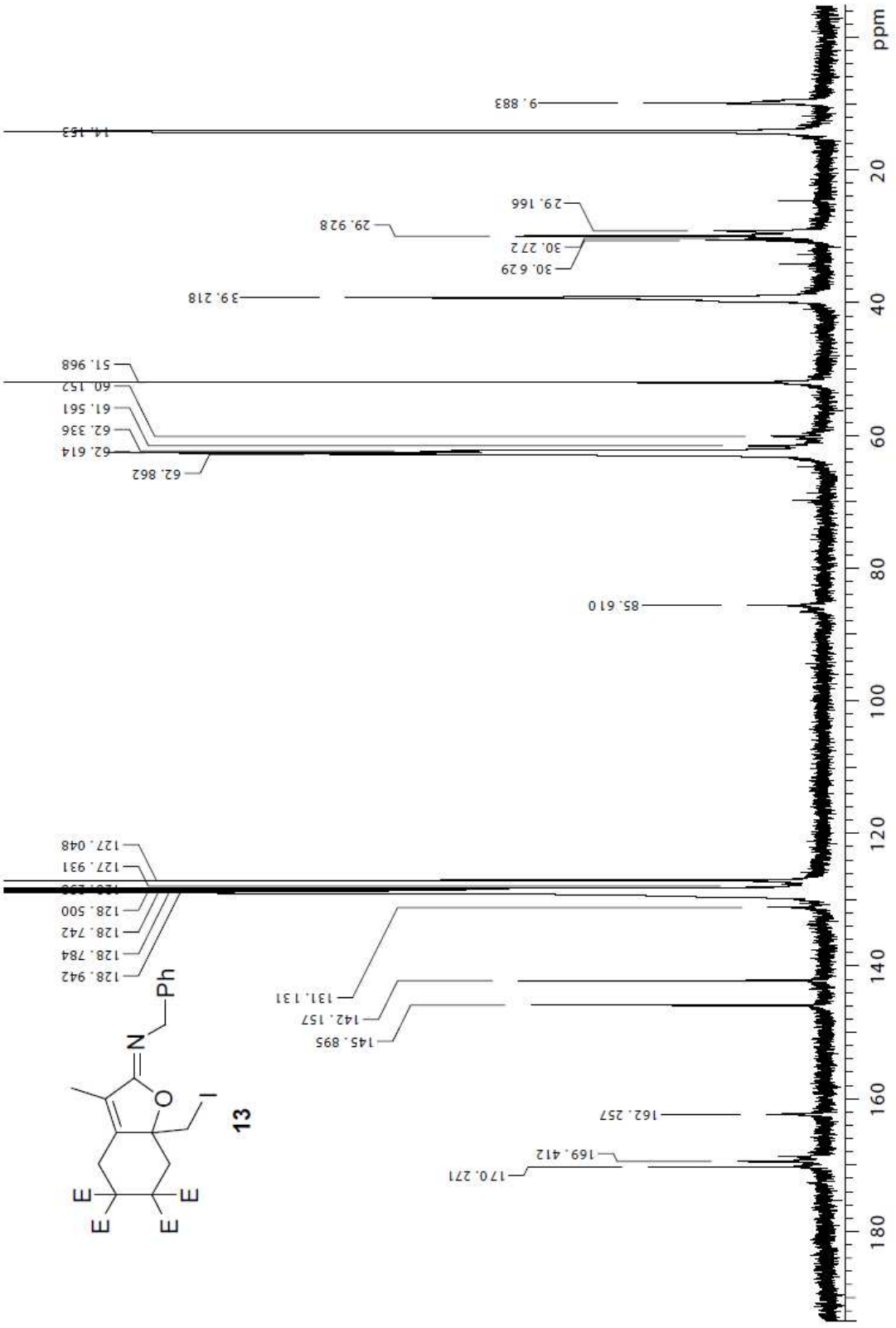
7.191
7.173
5.865
2.955
2.915
ppm
11


H
H
E
E
E
N
E
E
O
11
1 K
sec
15827 MHz
min, 37 sec
F2
(ppm)
2
3
4
5
6
7
8
220
200
180
160
140
120
100
80
60
40
20
0
F1 (ppm)


12
Ph
N
O
Br
E
E
E
E
7.592
7.576
7.255
7.236
7.217
7.161
7.125
7.107
4.895
4.856
4.795
4.756
4.113
4.058
4.006
3.996
3.925
3.907
3.889
3.871
3.311
3.277
3.226
3.101
1.787
1.656
0.997
0.945
0.927
0.919
0.909
0.867
ppm


ppm
20
40
60
80
100
120
140
160
180
9.877
14.147
29.268
29.922
30.623
39.224
51.962
60.140
61.555
62.378
62.620
62.862
85.628
127.036
127.919
128.258
128.500
128.742
128.778
128.935
131.149
142.157
145.871
162.238
169.388
170.259
Ph
N
O
Br
E
E
E
E
12


Ph
N
O
I
E
E
E
E
13
ppm
1
2
3
4
5
6
7
8


ppm
20
40
60
80
100
120
140
160
180
9.883
14.153
29.166
29.928
30.272
30.629
39.218
51.968
60.152
61.561
62.336
62.614
62.862
85.610
127.048
127.931
128.500
128.742
128.784
128.942
131.131
142.157
145.895
162.257
169.412
170.271
Ph
N
O
I
E
E
E
E
13