Supporting Information for

A Straighforward Access To Highly Substituted 2,3-DihydroBenzo*[b]*Oxepines by Ring Expansion of Benzopyryliums with Donor-Acceptor Diazo Compounds

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List of Abbreviations

PE	Petroleum Ether	DCM	Dichloromethane
EtOAc	Ethyl acetate	TFA	Trifluoroacetic acid
TMS	Trimethylsilyl		

1. General Methods

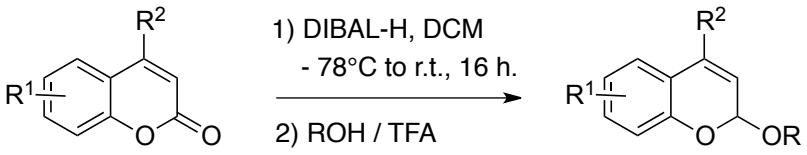
Technical grade solvents were used for quantitative flash chromatography. HPLC grade solvents purchased from Sigma-Aldrich or freshly distilled solvents were used for flash chromatography for compounds undergoing full characterization. Reaction solvents were purchased from ACROS 99.8% grade on molecular sieves. All other commercially available reagents were purchased from Acros, Aldrich, Fluka, VWR, Aplichem or Merck and used without any further purification. Flash chromatography was performed on silica gel (60-240 mesh) unless otherwise specified. Analytical thin layer chromatography (TLC) was performed on silica gel plates (Merck $60F_{254}$) visualized either with a UV lamp (254 nm) or by using permanganate stain. Organic extracts were dried over anhydrous $MgSO_4$. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance-III, at 300 MHz (^1H value) or 75 MHz (^{13}C value) in $CDCl_3$. Spectra were referenced to residual chloroform (7.26 ppm, ^1H; 77.0 ppm, ^{13}C) or TMS. Chemical shifts are reported in ppm, multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qt (quintet), and m (multiplet or unresolved), br (broad signal). Coupling constants, *J*, are reported in hertz (Hz). All NMR spectra were obtained at 300K unless otherwise specified.

Phenyldiazo-esters compounds were synthesized according literature procedure.[1]
4-phenyl-2*H*-chromene **1** was synthesized according literature procedure from **a**.[2]

[1] X. Luo, G. Chen, L. He, X. Huang, *J. Org. Chem.* **2016**, *81*, 2943-2949
[2] H. D. Srinivas, P. Maity, G. P. A. Yap, M. P. Watson, *J. Org. Chem.* **2015**, *80,* 4003-4016.

2. Synthesis of 4-Phenyl-coumarin Acetals 1b to 1d and 20.

General Procedure for the synthesis of 4-phenyl-2*H*-chromen-2-enes 1b-d and 20



a	R^1 = H; R^2 = Ph	**20**	R^1 = H; R^2 = Ph; R = *i*Pr
b	R^1 = 6-*t*Bu; R^2 = Ph	**1b**	R^1 = 6-*t*Bu; R^2 = Ph; R = Me
c	R^1 = 6-OMe; R^2 = Ph	**1c**	R^1 = 6-OMe; R^2 = Ph; R = Me
d	R^1 = 7-Cl; R^2 = Ph	**1d**	R^1 = 7-Cl; R^2 = Ph; R = Me
e	R^1 = H; R^2 = ≡—Ph	**1e**	R^1 = H; R^2 = ≡—Ph ; R = Me

4-phenyl-2*H*-chromen-2-enes **1b** to **1d** were synthesized from corresponding known 4-phenyl-chromenones **b,**[3] **c,**[4] **d**,[5] and **e**.[6]

To a stirred solution of 4-phenyl-chromenone (1.5 mmol) in dry DCM (10 mL), was added DIBAL-H (1.1 eq, 1M in heptane) over 1h at -78°C under argon atmosphere. The reaction was stirred 6h at -78°C. The cooling bath was removed and the reaction was stirred for additional 10h at r.t. The reaction was quenched by addition of a 2M Rochelle's salt aqueous solution and the aqueous layer was extracted 3 times with DCM (20 mL). The combined organic phases were dried over $MgSO_4$ and the solvents removed *in vacuo*. The crude colorless oil was directly engaged in the next step without purification.

The crude oil obtained was dissolved in suitable alcohol (MeOH or *i*PrOH) (10 mL) and few drops of trifluoroacetic acid were carefully added to the reaction mixture at r.t upon vigorous stirring. After 3h the reaction was completed and was quenched by addition of a spatula of solid K_2CO_3. The suspension was filtered and the filter cake washed with MeOH. Rotary evaporation of the solvent gave a crude solid which was purified by flash silica gel chromatography with PE/EtOAc/Et_3N : 80/19/1 as eluent.

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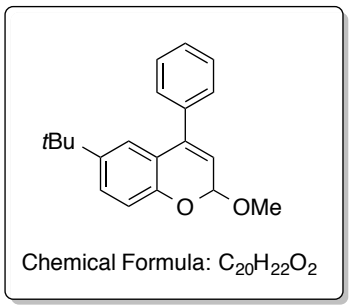
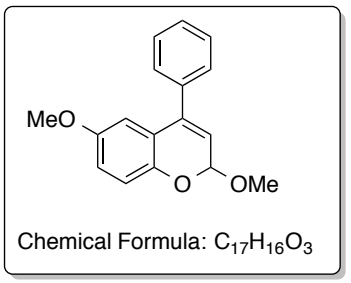
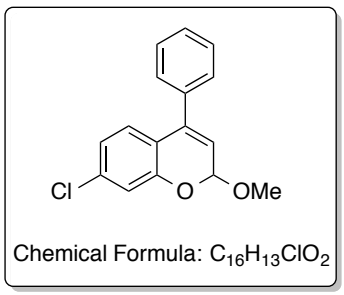
[3] R. Li, S. R. Wang, W. Lu, *Org. Lett.* **2007**, *9*, 2219-2222.
[4] M. Peggoty, G. Breuzard, A. Pagano, D. Allegro, V. Peyrot, K. Chibale, *Bioorg. Med. Chem.* **2017**, 25, 1652-1665.
[5] J. Li, H. Chen, D. Zhang-Negrerie, Y. Du, K. Zhao, *RSC Adv.* **2013**, *3*, 4311-4320.
[6] Y. Luo, J. Wu, *Tetrahedron* **2009**, *65*, 6810-6814.



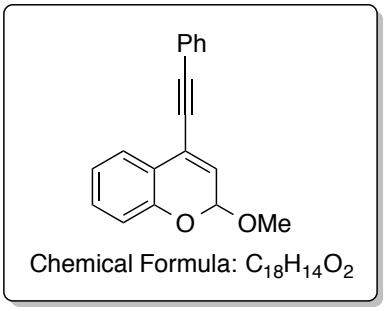
6-(*tert*-butyl)-2-methoxy-4-phenyl-2*H*-chromene **1b** was synthesized according general procedure. (1.4 mmol, 400 mg) of 6-(*tert*-butyl) -4-phenyl-chromenone **b** was used to give desired product as a white powder. (250 mg) 60%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.48-7.41 (m, 5H), 7.20 (dd, J_1= 2.6 Hz, J_2= 8.5 Hz, 1H), 7.09 (d, J= 2.6 Hz, 1H), 6.94 (d, J= 3.0 Hz, 1H), 5.76 (d, J= 4.3 Hz, 1H), 5.52 (d, J= 4.3 Hz, 1H), 3.43 (s, 3H), 1.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 149.3, 144.1, 139.2, 137.9, 128.9 (2C), 128.4 (2C), 128.2, 126.5, 123.2, 120.9, 117.9, 116.4, 95.9, 55.2, 34.3, 31.5 (3C); HRMS $[M+H]^+$ calc for $C_{20}H_{23}O_2$ 295.1693; found 295.1695.



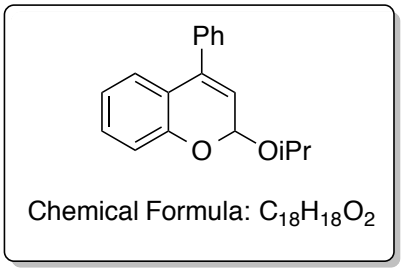
6-(methoxy)-2-methoxy-4-phenyl-2*H*-chromene **1c** was synthesized according general procedure. (1.2 mmol, 300 mg) of 6-(methoxy)-4-phenyl-chromenone **c** was used to give desired product as a white powder. (230 mg) 71%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38-7.27 (m, 5H), 6.95 (d, J= 8.5 Hz, 1H), 6.75 (dd, J_1= 3.0 Hz, J_2= 8.5 Hz, 1H), 6.61 (d, J= 3.0 Hz, 1H), 5.80 (d, J= 4.0 Hz, 1H), 5.51 (d, J= 4.0 Hz, 1H), 3.58 (s, 3H). 3.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 154.1, 145.4, 138.8, 137.5, 128.8 (2C), 128.4 (2C), 128.2, 122.4, 118.6, 117.6, 115.1, 111.5, 95.7, 55.8, 55.3; HRMS $[M+H]^+$ calc 269.1172; found 269.1169.



7-(chloro)-2-methoxy-4-phenyl-2*H*-chromene **1d** was synthesized according general procedure. (1.56 mmol, 400 mg) of 7-(chloro) -4-phenyl-chromenone **d** was used to give desired product as a white powder. (340 mg) 80%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.38-7.25 (m, 5H), 6.15-5.88 (m, 3H), 5.78 (d, J= 4.0Hz, 1H), 5.52 (d, J= 4.0Hz, 1H), 3.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.1, 138.1, 136.9, 129.3, 128.8 (2C), 128.6 (2C), 128.5, 126.5, 125.9, 123.2, 118.9, 118.5, 95.9, 55.4. HRMS $[M+H]^+$ calc 273.0677; found 273.0678.



2-methoxy-4-(phenylethynyl)-2*H*-chromene **1e** was synthesized according general procedure. (1 mmol, 246 mg) of 4-(phenylethynyl)-chromenone **e** was used to give desired product as a yellow oil. (182 mg) 69%. ^{1}H NMR ($CDCl_3$, 300 MHz): 7.60 (dd, J_1 = 7.7Hz, J_2 = 1.65Hz, 1H), 7.49-7.43 (m, 2H), 7.30-7.23 (m, 2H), 7.23-7.13 (m, 1H), 7.00-6.91 (m, 2H), 6.12 (d, *J*= 4.3 Hz, 1H) 5.53 (d, *J*= 4.3Hz, 1H), 3.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 150.9, 131.8 (2C), 130.1, 128.9, 128.5 (2C), 126.1, 123.5, 122.6, 121.8, 121.4, 120.0, 116.8, 95.6, 93.8, 84.3, 55.2; HRMS $[M\text{-}OMe]^+$ calc 231.0804; found 231.0810.



2-isopropoxy-4-phenyl-2*H*-chromene **20** was synthesized according general procedure using *i*PrOH as solvent for the second step. (1 mmol, 222 mg) of 4-phenyl-2*H*-chromen-2-one **a** was used to give desired product as a coloress thick oil. (140 mg) 57%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.36-7.25 (m, 5H), 7.18-7.11 (m, 1H), 7.06 (dd, J_1 = 7.7Hz, J_2 = 1.65Hz, 1H), 6.95 (dd, J_1 = 8.2Hz, J_2 = 1.3Hz, 1H), 6.82 (dt, J_1 = 7.7Hz, J_2 = 1.3Hz, 1H), 5.7 (s, 2H), 4.11 (st, *J*= 6.5Hz, 1H), 1.18-1.10 (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 151.7, 138.3, 137.8, 129.3, 128.9 (2C), 128.3 (2C), 128.0, 126.2, 121.9, 121.2, 118.8, 117.1, 93.8, 70.7, 23.7, 22.4; HRMS: $[M\text{-}OiPr]^+$ calc 207.0804; found 207.0811.

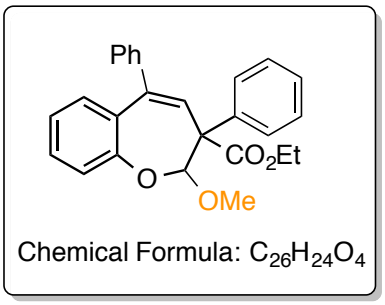
3. Synthesis of dihydrobenzo*[b]*oxepines 3 to 11 and 21

General Procedure:

In an oven-dried microwave vial under argon atmosphere, to a solution of 2-methoxy-4-phenyl-2*H*-chromene (0.25 mmol, 60 mg) in dry DCM (2.5 mL) was added ethyl 2-diazo-2-phenylacetate (0.3 mmol, 1.2 eq, 45 µL). Then TMSOTf (30 mol %, 13 µL) was carefully added dropwise at -15°C to the solution. Immediate gas evolution was observed and reaction was stirred at -15°C for further 30 min. The reaction was allowed to warm to room temperature and quenched by successive addition of Et_3N (100 µL) and water (2 mL). Aqueous phase was extracted with DCM (3x5 mL) and combined organic phases were washed with brine and dried over solid anhydrous Na_2SO_4. Evaporation of solvents gave a crude oil which was purified by column chromatography over silica gel (PE/EtOAc).

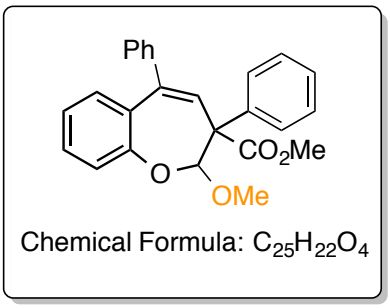
Procedure for 1 mmol scale synthesis of 3:

In an oven-dried microwave vial under argon atmosphere, to a solution of 2-methoxy-4-phenyl-2*H*-chromene (1.0 mmol, 238 mg) in dry DCM (10.0 mL) was added ethyl 2-diazo-2-phenylacetate (1.2 mmol, 1.2 eq, 228 mg). Then TMSOTf (30 mol %, 54 µL) was carefully added dropwise at -15°C to the solution. Immediate gas evolution was observed and reaction was stirred at -15°C for further 30 min. The reaction was allowed to warm to room temperature and quenched by successive addition of Et_3N (500 µL) and water (5 mL). Aqueous phase was extracted with DCM (3x15 mL) and combined organic phases were washed with brine and dried over solid anhydrous Na_2SO_4. Evaporation of solvents gave a crude oil, which was purified by column chromatography over silica gel (PE/EtOAc: 9/1) to give 87% (347 mg) of **3** as a thick yellow oil.



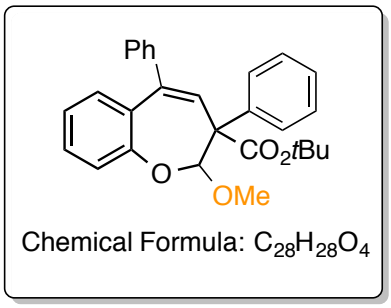
Chemical Formula: $C_{26}H_{24}O_4$

***Ethyl 2-methoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate* 3** was synthesized according general procedure from **2-methoxy-4-phenyl-2*H*-chromene 1** (0.25 mmol) to give 89% of an amorphous white solid (89 mg). d.r.: 2.8/1. R_f (PE/AcOEt 8/2) = 0.56; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers (noted: dia1 = minor / dia2 = major) δ 7.50-6.81 (m, 14H), 6.48 (d, *J*= 1.4Hz, 0.2H dia1), 6.08 (s, 0.8H, dia2), 5.79 (d, *J*= 1.4Hz, 0.2H dia1), 5.52 (s, 0.8H, dia2), 4.42-4.19 (m, 2H, dia1+dia2) 3.56 (s, 2.4H, dia2) 3.49 (s, 0.6H, dia1), 1.31 (t, *J*= 7.6Hz, 3H, dia1+dia2); ^{13}C NMR ($CDCl_3$, 75 MHz): 171.6/171.0 (dia1/dia2), 156.4/153.2 (dia1/dia2), 144.6/144.4 (dia1/dia2), 140.5/140.1 (dia1/dia2), 139.2/137.5 (dia1/dia2), 132.1/132.0 (dia1/dia2), 130.1 (2C) (dia1 or dia2), 129.5/129.4 (2C) (dia1/dia2), 129.3/129.2 (dia1/dia2), 129.1 (dia1 or dia2), 128.9/128.8 (dia1/dia2), 128.7/128.5 (dia1/dia2), 128.2/128.2 (2C), 127.6/127.5 (dia1/dia2), 127.5/127.4 (2C), 127.4/127.1 (dia1/dia2), 123.3/122.2 (dia1/dia2), 121.6/120.8 (dia1/dia2), 107.2/105.4 (dia1/dia2), 65.2/63.1 (dia1/dia2), 61.4 (dia1 or dia2), 57.7/57.3 (dia1/dia2), 14.2/14.1 (dia1/dia2); HRMS $[M+NH_4]^+$ calc. 418.2013; found 418.2016.



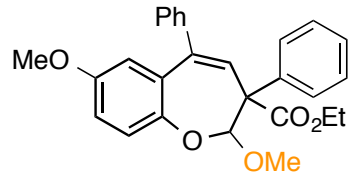
Chemical Formula: $C_{25}H_{22}O_4$

***Methyl 2-methoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate* 4** was synthesized according general procedure from **2-methoxy-4-phenyl-2*H*-chromene 1** (0.25 mmol) to give 79 % of a colorless oil (70 mg). d.r.: 2.1/1; R_f (PE/AcOEt 8/2) = 0.61; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers (noted : dia1 = minor / dia2 = major) δ 7.46-6.72 (m, 14H), 6.31 (s, 0.3H, dia1), 5.89 (s, 0.7H, dia2), 5.60 (s, 0.3H, dia1), 5.41 (s, 0.7H, dia2), 3.70 (s, 2H, dia2), 3.66 (s, 1H, dia1), 3.42 (s, 2H, dia2), 3.36 (s, 1H, dia1). ^{13}C NMR ($CDCl_3$, 75 MHz): 172.2 (2C) (dia1+dia2), 156.3/153.3 (dia1/dia2), 144.5/144.3 (dia1/dia2), 140.6/140.3 (dia1/dia2), 139.1/137.4 (dia1/dia2), 132.1/132.0 (dia1/dia2), 130.0 (2C), 129.4/129.3 (4C) (dia1/dia2), 129.1 (2C), 128.9 (2C), 128.6 (2C), 128.2/128.2 4C (dia1/dia2), 127.7/127.6/127.5/127.5/127.4/127.1 10C (dia1/dia2), 123.4/122.3 (dia1/dia2), 121.5/120.9 (dia1/dia2), 107.0/105.4 (dia1/dia2), 65.2/63.3 (dia1/dia2), 57.7/57.4 (dia1/dia2), 52.7/52.7 (dia1/dia2); HRMS $[M+NH_4]^+$ calc. 404.1856; found 404.1856.



Chemical Formula: $C_{28}H_{28}O_4$

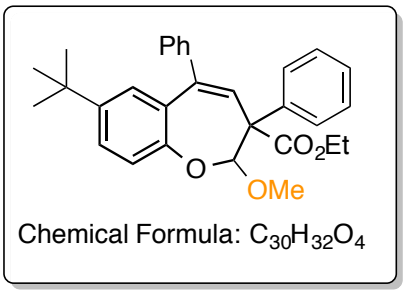
tert-butyl-2-methoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate **5** was synthesized according general procedure from **2-methoxy-4-phenyl-2*H*-chromene 1** (0.25 mmol) to give 79 % of a colorless oil (70 mg). d.r.: 1.8/1 ; R_f (PE/AcOEt 8/2) = 0.60; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers (noted : dia1 =minor / dia2 =major) δ 7.45-6.70 (m, 15H), 6.34 (d, *J*= 1.5Hz, 0.3H, dia1), 5.87 (s, 0.7H, dia2), 5.67 (d, *J*= 1.5Hz, 0.3H), 5.31 (s, 0.7H), 3.44 (s, 2H, dia2), 3.37 (s, 1H, dia1), 1.39 (s, 5.7H, dia2), 1.36 (s, 3.3H, dia1); ^{13}C NMR ($CDCl_3$, 75 MHz): 170.5/169.9 (dia1/dia2), 156.7/153.1 (dia1/dia2), 144.7/144.6 (dia1/dia2), 140.1, 139.7/139.3 (dia1/dia2), 137.9, 132.1/131.9 (dia1/dia2), 130.2/130.1 (2C) (dia1/dia2), 129.9, 129.5/129.4 (2C) (dia1/dia2), 129.2/129.1 (dia1/dia2), 128.9/128.6 (dia1/dia2), 128.4/128.3 (2C) (dia1/dia2), 128.1/127.5 (dia1/dia2), 127.3/127.3 (2C) (dia1/dia2), 127.3/127.0 (dia1/dia2), 123.3/122.2 (dia1/dia2), 121.7/120.8 (dia1/dia2), 107.6/105.7 (dia1/dia2), 82.1/82.0 (dia1/dia2), 65.8/63.3 (dia1/dia2), 57.8/57.3 (dia1/dia2), 28.1/28.0 (3C) (dia1/dia2); HRMS $[M+NH_4]^+$ calc. 446.2326; found 446.2330.



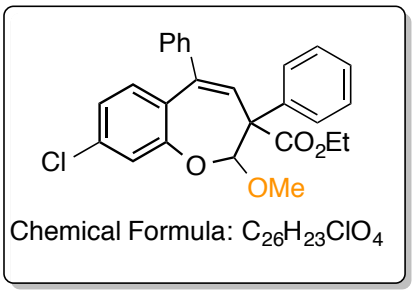
Chemical Formula: $C_{27}H_{26}O_5$

Ethyl 2,7-dimethoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate **6** was synthesized according general procedure from **2,6-dimethoxy-4-phenyl-2*H*-chromene 1c** (0.25 mmol) to give 78 % of a colorless oil (68 mg). d.r.: 1/1; R_f (PE/AcOEt 8/2) = 0.44; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers (noted : dia1 = minor / dia2 = major) δ 7.42-7.11 (m, 10H), 6.99 (d, *J*= 8.8Hz, 0.5H, dia2), 6.87 (d, *J*= 8.8Hz, 0.5H, dia1), 6.73-6.60 (m, 1H, dia1+dia2), 6.43-6.37 (m, 1H, dia1+dia2), 6.34 (d, *J*= 1.4Hz, 0.5H, dia1), 5.92 (s, 0.5H, dia2), 5.56 (d, *J*= 1.4Hz, 0.5H, dia1), 5.36 (s, 0.5H, dia2), 4.29-4.02 (m, 2H, dia1+dia2), 3.53 (s, 1.5H, dia2), 3.48 (s, 1.5H, dia1), 3.42 (s, 1.5H, dia2), 3.38 (s, 1.5H, dia1), 1.22-1.09 (m, 3H, dia1+dia2). ^{13}C NMR ($CDCl_3$, 75 MHz): 171.6/170.9 (dia1/dia2), 155.2/154.4 (dia1/dia2), 150.4/147.1 (dia1/dia2), 144.3/144.1 (dia1/dia2), 140.3/139.6 (dia1/dia2), 139.4/137.5 (dia1/dia2), 130.0 (2C), 129.9/129.8 (dia1/dia2), 129.7/129.7 (dia1/dia2), 129.5/129.4 (4C dia1/dia2), 128.5 (2C), 128.2/128.2 (4C dia1/dia2), 127.6/127.5/127.4 (7C), 127.2, 122.3/121.4 (dia1/dia2), 117.1/116.9 (dia1/dia2), 114.4/114.3 (dia1/dia2), 107.4/105.5 (dia1/dia2), 65.2/63.3 (dia1/dia2), 61.5/61.5 (dia1/dia2),

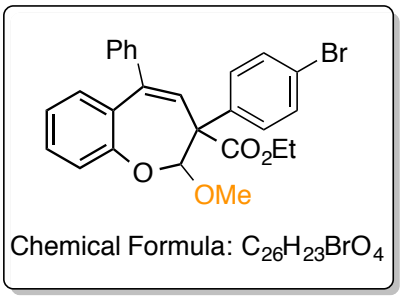
57.7/57.3 (dia1/dia2), 55.6/55.4 (dia1/dia2), 14.2/14.1 (dia1/dia2); HRMS [M+ NH_4]$^+$ calc. 448.2118; found 448.2126.



Ethyl 7-(tert-butyl)-2-methoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate **7** was synthesized according general procedure from **6-(*tert*-butyl)-2-methoxy-4-phenyl-2*H*-chromene 1b** (0.20 mmol) to give 81 % of a colorless oil (74 mg). d.r.: 1.3/1; R_f (PE/AcOEt 8/2) = 0.56; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers (noted : dia1 = minor / dia2 = major) δ 7.46-6.83 (m, 14H), 6.33 (d, *J*= 1.6Hz, 0.4H, dia1), 5.89 (s, 0.6H, dia2), 5.60 (d, *J*= 1.6Hz, 0.4H, dia1), 5.38 (s, 0.6H, dia2), 4.30-4.00 (m, 2H, dia1+dia2), 3.44 (s, 1.6H, dia2), 3.32 (s, 1.4H, dia1), 1.22-1.14 (m, 3H), 1.06 (s, 5H, dia2), 1.02 (s, 4H, dia1). ^{13}C NMR ($CDCl_3$, 75 MHz): 171.7/171.0 (dia1/dia2), 154.3/150.9 (dia1/dia2), 145.8/144.7 (dia1/dia2), 144.6/144.4 (dia1/dia2), 140.9/140.2 (dia1/dia2), 139.5/137.5 (dia1/dia2), 130.2/129.5/129.5/129.3/129.1/128.9/128.8/128.5/128.3/128.3/128.1/128.0/127.9/127.8/127.6/127.5/127.4/127.1/126.7/126.2/125.8 (14C) (dia1/dia2), 121.0/120.0 (dia1/dia2), 107.2/105.5 (dia1/dia2), 65.3/63.2 (dia1/dia2), 61.5/61.4 (dia1/dia2), 57.8/57.3 (dia1/dia2), 34.3/34.2 (dia1/dia2), 31.3/31.2 (3C) (dia1/dia2), 14.2/14.1 (dia1/dia2); HRMS [M+NH_4]$^+$ calc. 474.2639; found 474.2639.

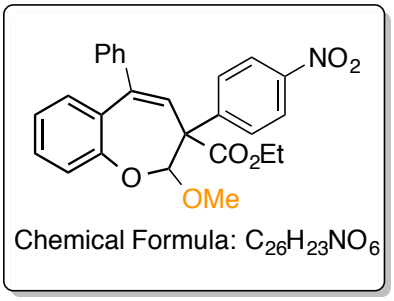


Ethyl 8-chloro-2-methoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate **8** was synthesized according general procedure from **7-(chloro)-2-methoxy-4-phenyl-2*H*-chromene 1d** (0.20 mmol) to give 83 % of a colorless oil (72 mg). d.r.: 3.8/1; R_f (PE/AcOEt 8/2) = 0.55; ^{1}H NMR ($CDCl_3$, 300 MHz): δ mixture of diastereoisomers (noted : dia1 = minor / dia2 = major) 7.40-7.15 (m, 11H), 7.10 (dd, J_1= 3.9Hz, J_2= 8.5Hz, 1H), 7.00 (d, *J*= 8.5Hz, 1H), 6.87-6.81 (m, 1H), 6.41 (d, *J*= 1.4Hz, 0.2H, dia1), 5.97 (s, 0.8H, dia2), 5.70 (d, *J*= 1.4Hz, 0.2H, dia1), 5.48 (s, 0.8H, dia2), 4.27-4.08 (m, 2H, dia1+dia2), 3.40 (s, 2.5H, dia2), 3.36 (s, 0.5H, dia1), 1.22-1.12 (m, 3H, dia1+dia2); ^{13}C NMR ($CDCl_3$, 75 MHz): 171.3, 154.7, 143.6, 139.4, 137.2, 131.4, 130.7, 130.6, 129.8 (2C), 129.3 (2C), 129.0, 128.6, 128.5 (2C), 127.7, 127.6 (2C), 127.4, 122.3, 107.2, 65.0, 61.6, 57.5, 14.1; HRMS [M+NH_4]$^+$ calc. 452.1623; found 452.1613.



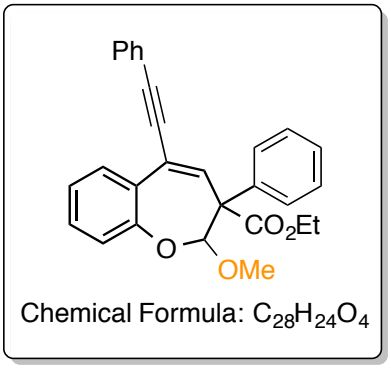
Chemical Formula: $C_{26}H_{23}BrO_4$

Ethyl 3-(4-bromophenyl)-2-methoxy-5-phenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate **9** was synthesized according general procedure from **2-methoxy-4-phenyl-2*H*-chromene 1** (0.20 mmol) to give 60% of an amorphous white solid (70 mg). d.r.: 5/1; R_f (PE/AcOEt 8/2) = 0.53; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers δ (noted : dia1 = minor / dia2 = major) 7.51-6.95 (m, 12H), 6.95-6.72 (m, 2H), 6.31 (s, 0.2H, dia1), 5.80 (s, 0.8H, dia2), 5.63 (s, 0.2H, dia1), 5.36 (s, 0.8H, dia2), 4.30-4.05 (m, 2H, dia1 + dia2), 3.45 (s, 2.5H, dia2), 3.36 (s, 0.5H, dia1), 1.23-1.14 (m, 3H, dia1 + dia2); ^{13}C NMR ($CDCl_3$, 75 MHz): 171.1, 156.5, 144.1, 141.1, 136.4, 132.2 (2C, dia1), 132.1 (2C, dia2), 131.6, 130.5 (2C), 129.5 (2C, dia1), 129.4, 129.4 (2C, dia2), 129.3, 128.8, 128.4 (2C, dia1), 128.3 (2C, dia2), 127.5, 123.5, 122.0, 120.7, 107.0, 65.0, 61.7, 57.3, 14.2; HRMS $[M+H]^+$ calc. 479.0852; found 479.0858.



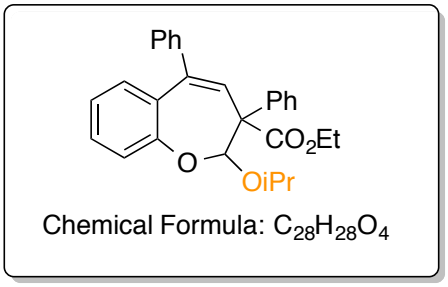
Chemical Formula: $C_{26}H_{23}NO_6$

Ethyl 3-(4-nitrophenyl)-2-methoxy-5-phenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate **10** was synthesized according general procedure from **2-methoxy-4-phenyl-2*H*-chromene 1** (0.20 mmol) to give 71% of yellow oil (77 mg). d.r.: 3.9/1; R_f (PE/AcOEt 8/2) = 0.46; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers (noted: dia1 = minor / dia2 = major) δ 8.22-8.10 (m, 2H, dia1+ dia2), 7.67 (d, *J*= 9.0Hz, 0.5H, dia1), 7.59 (d, *J*= 9.0Hz, 1.5H, dia2), 7.46-7.21 (m, 6H), 7.19-7.09 (m, 1H), 7.06-6.86 (m, 2H), 6.43 (d, *J*= 1.3Hz, 0.2H, dia1), 5.88 (s, 0.8H, dia2), 5.81 (d, *J*= 1.3Hz, 0.8H, dia2), 5.49 (s, 0.8H, dia2), 4.41-4.20 (m, 2H, dia1 + dia2), 3.55 (s, 2.3H, dia2), 3.48 (s, 0.7H, dia1), 1.34-1.22 (m, 3H, dia1 + dia2).^{13}C NMR ($CDCl_3$, 75 MHz): 170.5, 156.5, 147.2, 144.6, 143.8, 141.9, 132.4/132.2 (dia1/dia2), 131.6 (2C dia2), 129.8 (2C dia1), 129.3 (2C dia2), 128.7, 128.5, 128.4 (2C dia2), 128.3, 128.2, 127.7 (2C dia1), 127.4/127.3 (dia1/dia2), 123.8/123.6 (dia1/dia2), 122.3, 121.5/120.6 (dia1/dia2), 106.8, 65.5/63.0 (dia1/dia2), 62.2/62.0 (dia1/dia2), 57.7/57.2 (dia1/dia2), 14.2; HRMS $[M+NH_4]^+$ calc. 463.1864; found 463.1863.



Chemical Formula: $C_{28}H_{24}O_4$

Ethyl 2-methoxy-3-phenyl-5-(phenylethynyl)-2,3-dihydrobenzo[b]oxepine-3-carboxylate **11** was synthesized according general procedure from **2-methoxy-4-phenyl-2*H*-chromene 1e** (0.25 mmol) to give 79 % of a colorless oil (70 mg). d.r.: 2.8/1; R_f (PE/AcOEt 8/2) = 0.51; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers (noted: dia1 =minor / dia2 =major) δ 8.12-7.99 (dd, J_1= 2.0Hz, J_2= 8.0Hz, 1H, dia1+dia2), 7.54-7.44 (m, 2H), 7.35-7.06 (m, 12H), 6.91 (dd, J_1= 1.7Hz, J_2= 8.0Hz, 0.33H, dia1), 6.51 (s, 0.66H, dia2), 5.71 (d, *J*= 1.7Hz, 0.33H, dia1), 5.35 (s, 0.66H, dia2), 4.22 (q, *J*= 7.2Hz, 2H, dia1+dia2), 3.38 (s, 2H, dia2), 3.32 (s, 1H, dia1), 1.26-1.12 (m, 3H, dia1+dia2) ; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.8/170.4 (dia1/dia2), 154.9/151.7 (dia1/dia2), 138.6/137.1 (dia1/dia2), 134.6/134.4 (dia1/dia2), 131.6/131.5 (2C) (dia1/dia2), 131.3, 129.9/129.9 (2C) (dia1/dia2), 129.7, 128.8/128.6 (dia1/dia2), 128.5/128.4 (dia1/dia2), 128.4/128.3 (2C) (dia1/dia2), 127.9/127.7 (dia1/dia2), 127.6/127.3 (2C) (dia1/dia2), 126.1/125.5 (dia1/dia2), 123.7/123.3 (dia1/dia2), 123.1/123.0 (dia1/dia2), 122.9/122.6 (dia1/dia2), 121.6/120.9 (dia1/dia2), 105.7/103.1 (dia1/dia2), 90.2/90.0 (dia1/dia2), 89.2/89.2 (dia1/dia2), 65.5/63.8 (dia1/dia2), 62.0/61.8 (dia1/dia2), 57.7/57.3 (dia1/dia2), 14.1; HRMS $[M+Na+MeCN]^+$ calc. 488.1838; found 488.1832.



Chemical Formula: $C_{28}H_{28}O_4$

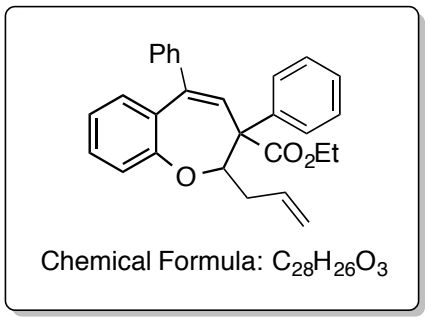
Ethyl 2-isopropoxy-3,5-diphenyl-2,3-dihydrobenzo[*b*]oxepine-3-carboxylate ***21*****.** was synthesized according general procedure from **2-isopropoxy-4-phenyl-2*H*-chromene 20** (0.25 mmol), to give 78% of desired product as a yellow oil. (84 mg). d.r.: 1.1/1; R_f (PE/AcOEt 8/2) = 0.64; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers (noted: dia1 =minor / dia2 =major) δ 7.52-7.45 (m, 1H), 7.43-7.04 (m, 10H), 6.97-6.79 (m, 3H), 6.42 (d, *J*= 1.5Hz, 0.45H dia1), 6.01 (s, 0.45H, dia1), 5.96 (d, *J*= 1.5Hz, 0.55H, dia2), 5.7 (s, 0.55H, dia2), 4.31-4.13 (m, 2H, dia1+dia2), 4.01-3.88 (m, 1H, dia1+dia2), 1.33 (t, *J*= 7.0Hz, 3H, dia1+dia2), 1.14-0.76 (m, 6H, dia1+dia2) ; ^{13}C NMR ($CDCl_3$, 75 MHz): δ 171.7/171.1 (dia1/dia2), 155.7/153.3 (dia1/dia2), 144.9/144.7 (dia1/dia2), 140.4/140.1 (dia1/dia2), 139.5/137.9 (dia1/dia2), 132.0/131.8 (dia1/dia2), 129.8/129.5 (dia1/dia2) (2C), 129.4/129.3 (dia1/dia2), 129.0/128.9 (dia1/dia2), 128.6/128.5 (dia1/dia2), 128.5/128.4 (dia1/dia2), 128.2/128.2 (dia1/dia2) (2C), 127.6/127.4

(dia1/dia2), 127.5/127.3 (dia1/dia2) (2C), 127.3/127.1 (dia1/dia2); 127.0 (dia1+dia2), 123.0/121.9 (dia1/dia2), 121.7/121.3 (dia1/dia2), 103.0/101.0 (dia1/dia2), 71.3/71.0 (dia1/dia2), 65.2/63.3 (dia1/dia2), 61.6/61.4 (dia1/dia2), 22.9/22.6 (dia1/dia2), 20.9 (dia1+dia2), 14.2/14.1 (dia1/dia2); HRMS $[M\text{-}OiPr]^+$ calc. 369.1487; found 369.1497.

4. Synthesis of dihydrobenzo*[b]*oxepines 12 to 16

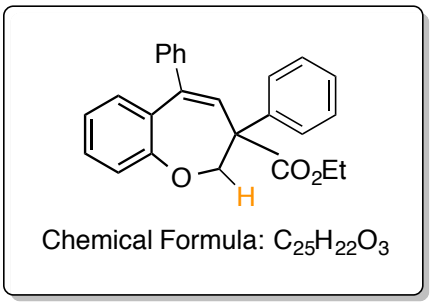
General Procedure:

In a oven-dried microwave vial under argon atmosphere, to a solution of 2-methoxy-4-phenyl-2*H*-chromene (0.25 mmol, 60 mg) in dry DCM (2.5 mL) was added ethyl 2-diazo-2-phenylacetate (0.3 mmol, 1.2 eq, 45 µL). Then TMSOTf (30 mol%, 13 µL) was carefully added dropwise at -15°C to the solution. Immediate gas evolution was observed and reaction was stirred at -15°C for further 30 min. To the resulting solution was added, $TiCl_4$ (2.2 eq, 0.55 mmol, 60 µL) dropwise, the reaction turned to a bright red color and suitable nucleophile (5 eq) was added dropwise at -15°C. The reaction was stirred for further 30min at -15°C after what the ice/salt bath was removed and the reaction was stirred 1h at room temperature. The reaction mixture was quenched by successive addition of Et_3N (200 µL), MeOH (500 µL), water (1 mL), HCl 6N (500 µL) and finally diluted with DCM (2mL). Aqueous phase was extracted with DCM (3x5 mL) and combined organic phases were washed with brine and dried over solid anhydrous Na_2SO_4. Evaporation of solvents gave a crude oil, which was purified by column chromatography over silica gel (PE/EtOAc).



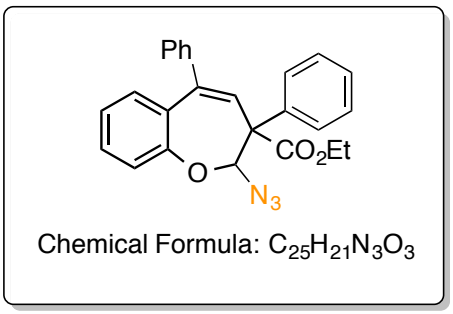
Chemical Formula: $C_{28}H_{26}O_3$

Ethyl 2-allyl-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate **12** was synthesized according general procedure from **2-methoxy-4-phenyl-2*H*-chromene 1** (0.25 mmol) using allyltrimethylsilane as nucleophile (1.25 mmol, 5 eq, 200 µL) to give 84 % of a colorless oil (86 mg). d.r.: 3.2/1; R_f (PE/AcOEt 8/2) = 0.65; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers (noted: dia1 = minor / dia2 = major) δ 7.34-7.19 (m, 10H) , 7.13-6.76 (m, 4H), 6.28-6.20 (1H, dia1+dia2), 5.81-5.64 (m, 1H, dia1+dia2), 4.98-4.84 (m, 2H, dia1+dia2), 4.36-4.28 (m, 1H, dia1+dia2), 4.28-4.08 (m, 2H, dia1+dia2), 3.15-3.01 (m, 1H), 2.07-1.98 (m, 1H), 1.20-1.12 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): 171.4, 159.1, 144.7, 140.3, 138.8, 135.7, 133.3, 132.2, 129.5 (2C), 128.9, 128.8 (2C), 128.2 (2C), 127.7, 127.5, 127.3 (2C), 127.1, 122.2, 121.1, 117.0, 86.2, 63.8, 61.3, 35.7, 14.1; HRMS $[M+H]^+$ calc. 428.2220; found 428.2222.



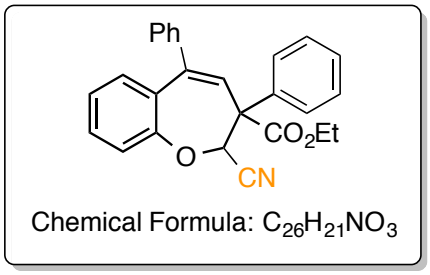
Chemical Formula: $C_{25}H_{22}O_3$

Ethyl 3,5-diphenyl-2,3-dihydrobenzo[b]oxepin-3-carboxylate **13** was synthesized according general procedure from **2-methoxy-4-phenyl-2*H*-chromene 1** (0.25 mmol) using triethylsilane as source of nucleophile (1.25 mmol, 5 eq, 200 µL) to give 91 % of a colorless oil (82 mg). R_f (PE/AcOEt 8/2) = 0.60; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.34-7.12 (m, 10H), 7.10-6.96 (m, 2H), 6.91-6.78 (m, 2H), 6.33 (d, *J*= 1.5Hz, 1H), 4.88 (dd, J_1= 1.5Hz, J_2= 12.0Hz, 1H), 4.24-4.10 (m, 2H), 4.02 (d, *J*= 12.0Hz, 1H), 1.13 (t, *J*= 7.5Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): 172.2, 160.8, 145.0, 139.8, 139.5, 132.8, 132.1, 130.2, 129.5 (2C), 128.9 (2C), 128.5, 128.2 (2C), 127.8, 127.2, 126.8 (2C), 123.0, 120.6, 77.8, 61.7, 60.9, 14.1; HRMS $[M+NH_4]^+$ calc. 388.1907; found 388.1920.



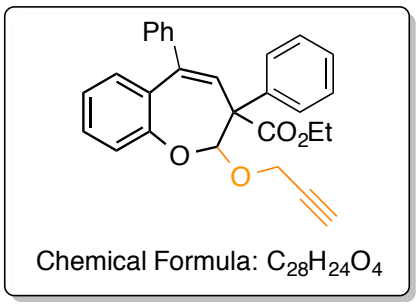
Chemical Formula: $C_{25}H_{21}N_3O_3$

Ethyl 2-azido-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate **14** was synthesized according general procedure from **2-methoxy-4-phenyl-2*H*-chromene 1** (0.1 mmol) using trimethylsilylazide as nucleophile (0.5 mmol, 5 eq, 65 µL) to give 88 % of a colorless oil (41 mg). d.r.: 4/1; R_f (PE/AcOEt 8/2) = 0.61; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers (noted: dia1 = minor / dia2 = major) δ 7.44-6.98 (m, 14H), 6.37 (s, 0.2H, dia1), 6.08 (s, 0.2H, dia1), 6.01 (s, 0.8H, dia2), 5.95 (s, 0.8H, dia2), 4.26-4.10 (m, 2H, dia1+dia2), 1.17 (t, *J*= 7.2Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): 171.0/170.4 (dia1/dia2), 156.6, 143.9/143.7 (dia1/dia2), 140.8, 136.7, 132.2/132.1 (dia1/dia2), 129.8/129.6 (2C) (dia1/dia2), 129.3/129.2 (2C) (dia1/dia2), 128.9/128.8 (dia1/dia2), 128.7, 128.3 (2C), 128.1/128.0 (dia1/dia2), 127.8/127.6, (2C) (dia1/dia2), 127.5, 124.2, 123.1, 121.3/121.1(dia1/dia2), 94.9/94.4 (dia1/dia2), 64.5, 62.0/61.9 (dia1/dia2), 14.1/14.0 (dia1/dia2); HRMS $[M+Na+ACN]^+$ calc. 475.1741; found 475.1741.



Chemical Formula: $C_{26}H_{21}NO_3$

Ethyl 2-cyano-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate **15** was synthesized according general procedure from **2-methoxy-4-phenyl-2*H*-chromene 1** (0.1 mmol) using trimethylsilylcyanide as nucleophile (0.5 mmol, 5 eq, 63 µL) to give 78 % of a colorless oil (35 mg). d.r.: 1:1; R_f (PE/AcOEt 8/2) = 0.49; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers δ 7.47-6.85 (m, 15H), 6.31 (s, 0.5H), 6.22 (s, 0.5H), 5.70 (s, 0.5H), 5.12 (s, 0.5H), 4.33-4.16 (m, 2H, dia1+dia2), 1.24-1.10 (m, 3H) ; ^{13}C NMR ($CDCl_3$, 75 MHz): 170.4/169.7 (dia1/dia2), 157.3/157.1 (dia1/dia2), 143.9/143.7 (dia1/dia2), 140.8/140.5 (dia1/dia2), 136.5/136.3 (dia1/dia2), 132.9/132.7 (dia1/dia2), 129.7/129.6 (2C) (dia1/dia2), 129.5, 129.3/129.2 (dia1/dia2), 128.9/128.8 (2C) (dia1/dia2), 128.4/128.1 (dia1/dia2), 127.7/127.7 (2C) (dia1/dia2), 127.3/127.3 (2C) (dia1/dia2), 124.8/124.4 (dia1/dia2), 121.4/121.0 (dia1/dia2), 114.8, 74.9, 63.0/62.8 (dia1/dia2), 62.6/62.5 (dia1/dia2), 14.0; HRMS $[M+H]^+$ calc. 413.1860; found 413.1863.



Chemical Formula: $C_{28}H_{24}O_4$

Ethyl 3,5-diphenyl-2-(prop-2-yn-1-yloxy)-2,3-dihydrobenzo[b]oxepine-3-carboxylate **16** was synthesized according general procedure from **2-methoxy-4-phenyl-2*H*-chromene 1** (0.1 mmol) using propargyl alcohol as nucleophile (0.5 mmol, 5 eq, 29 µL) to give 86 % of a colorless oil (41 mg). d.r.: 1/3; R_f (PE/AcOEt 8/2) = 0.48; ^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers (noted : dia1 = minor / dia2 = major) δ 7.44-7.01 (m, 11H), 6.96-6.71 (m, 3H), 6.45 (s, 0.75H, dia2), 6.06 (s, 0.75H, dia2), 5.91 (s, 0.25H, dia1), 5.76 (s, 0.25H, dia1), 4.38-4.06 (m, 4H), 2.33-2.25 (m, 1H), 1.26-1.06 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): 171.2/170.7 (dia1/dia2), 155.9/153.2 (dia1/dia2), 144.3/144.3 (dia1/dia2), 140.5/140.2 (dia1/dia2), 138.8/137.3 (dia1/dia2), 132.1/132.0 (dia1/dia2), 130.2, 129.4/129.2 (2C) (dia1/dia2), 129.0, 128.9/128.9 (dia1/dia2), 128.5/128.4 (2C) (dia1/dia2), 128.3/128.3 (dia1/dia2), 128.2/128.1 (2C) (dia1/dia2), 127.6/127.6 (dia1/dia2), 127.4/127.1 (2C) (dia1/dia2), 123.5/122.3 (dia1/dia2), 121.4/120.8 (dia1/dia2), 103.4/101.8 (dia1/dia2), 75.2/75.1 (dia1/dia2), 64.9/62.6 (dia1/dia2), 61.8/61.6 (dia1/dia2), 56.1/55.7 (dia1/dia2), 14.2/14.0 (dia1/dia2); HRMS $[M+NH_4]^+$ calc 442.2013; found 442.2017.

5. Protocol for diastereo-enrichment of 3 and single crystal growth.

- *Diastereo-enrichment of **3***

A minimal amount of **3** (342 mg) as a yellow oil was transferred to a vial. Small portions of diethyl ether (1 mL) were added to the oil to form a white precipitate, which was triturated with diethyl ether until disappearance of the yellow color. The white solid was dried under vacuum to give **3** (100 mg, 25%) with a diastereoisomeric ratio of 8.8:1 determined by ^{1}H NMR analysis.

^{1}H NMR ($CDCl_3$, 300 MHz): mixture of diastereoisomers (noted: dia1 = minor / dia2 = major) δ 7.50-6.81 (m, 14H), 6.48 (d, *J*= 1.4Hz, 0.1H dia1), 6.08 (s, 0.9H, dia2), 5.79 (d, *J*= 1.4Hz, 0.1H dia1), 5.52 (s, 0.9H, dia2), 4.42-4.19 (m, 2H, dia1+dia2) 3.56 (s, 2.7H, dia2) 3.49 (s, 0.3H, dia1), 1.31 (t, *J*= 7.6Hz, 3H, dia1+dia2);

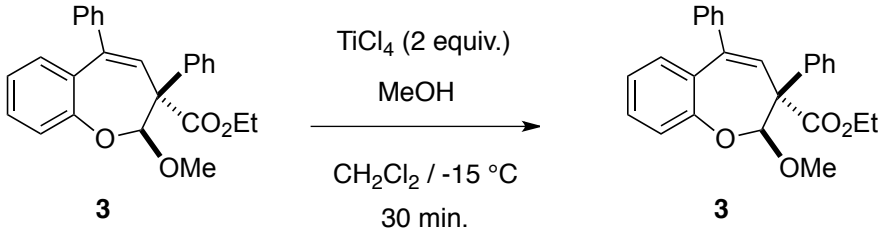
- *Crystal growth of **3***

A minimal amount of diastereo-enriched **3** (10 mg) was dissolved in HPLC grade diethyl-ether (5mL) and growth of a single crystal was observed upon slow evaporation of the solvent over 1 week.

The CIF file has been registered to the CCDC as number 1819307.

6. Protocols for mechanistic studies

- *$TiCl_4$-mediated transketalization of **3** with MeOH*

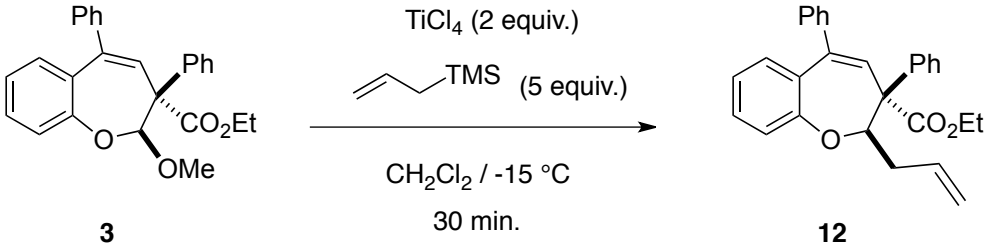


Entry	dr of starting **3**	dr of obtained **3**	Yield of **3** (%)
1	1.7:1	1.2:1	78
2	0.8:1	1.2:1	83

In a oven-dried microwave vial under argon atmosphere, to a solution of ***Ethyl 2-methoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate*** **3** (0.083 mmol, 33 mg) in dry DCM (2 mL) was carefully added $TiCl_4$ (2 eq, 12 µL) dropwise at -15°C then MeOH (500 µL). Reaction was stirred at -15°C for further 30 min. The reaction mixture was quenched by addition of water (1 mL), and finally diluted with DCM (2mL). Aqueous phase was extracted with DCM (3x5 mL) and combined organic phases were washed with brine and dried over solid anhydrous Na_2SO_4. Evaporation of solvents gave a crude oil which was purified by column chromatography over silica gel (PE/EtOAc: 9/1) to give **3** as a yellow oil.

-

*TiCl4-mediated allylation of **3** with allyl trimethysilane*

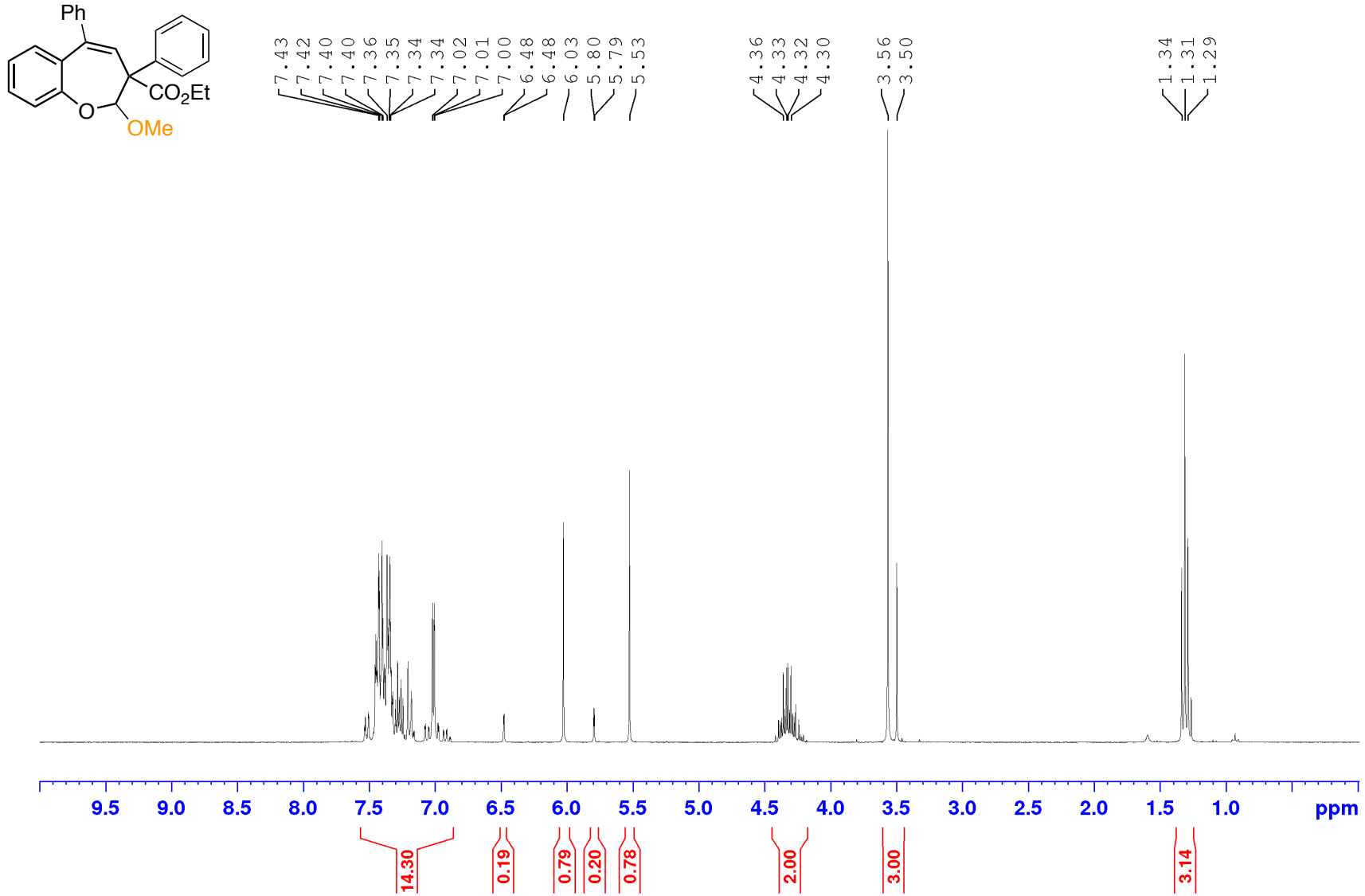


3 **12**

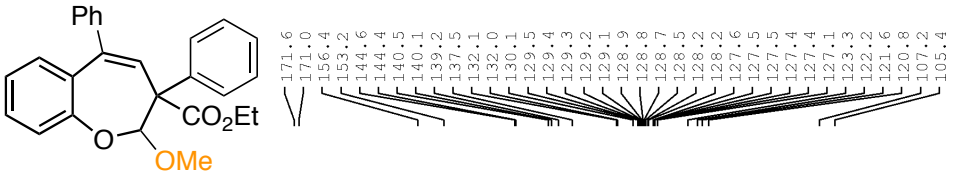
Entry	dr of starting **3**	dr of obtained **12**	Yield of **12** (%)
1	3.8:1	4.5:1	83
2	1.1:1	4.5:1	87

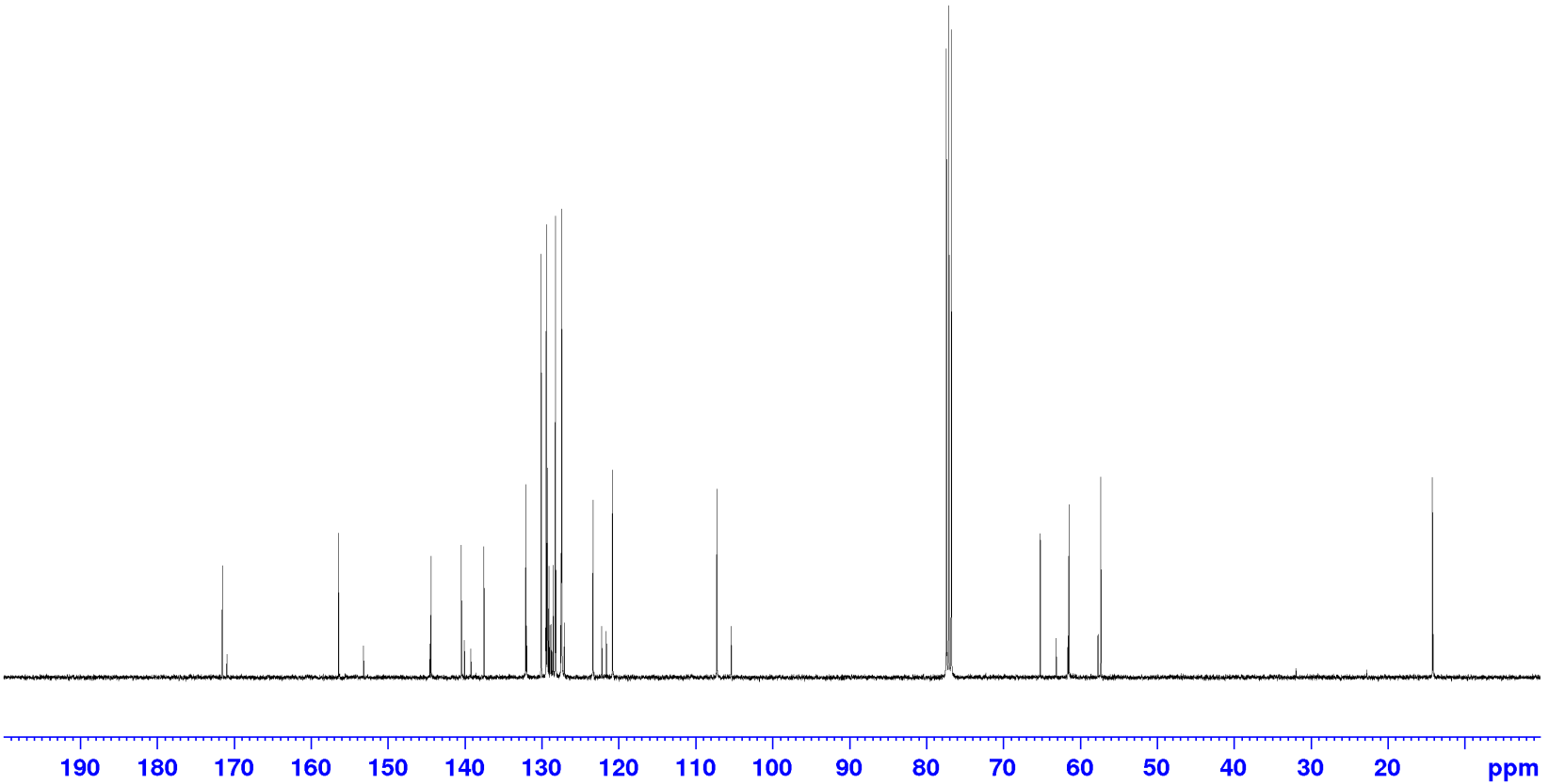
In a oven-dried microwave vial under argon atmosphere, to a solution of ***Ethyl 2-methoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate*** **3** (0.05 mmol, 20 mg) in dry DCM (1 mL) was added allyltrimethylsilane (0.25 mmol, 5 eq, 40 µL). Then $TiCl_4$ (2 eq, 12 µL) was carefully added dropwise at -15°C to the solution. Reaction was stirred at -15°C for further 30 min. The reaction mixture was quenched by successive addition of MeOH (500 µL), water (1 mL), and finally diluted with DCM (2mL). Aqueous phase was extracted with DCM (3x5 mL) and combined organic phases were washed with brine and dried over solid anhydrous Na_2SO_4. Evaporation of solvents gave a crude oil which was purified by column chromatography over silica gel (Pet. Ether/EtOAc: 99/1) to give **12** as a colorless oil.

ethyl 2-methoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate 3



ethyl 2-methoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate 3





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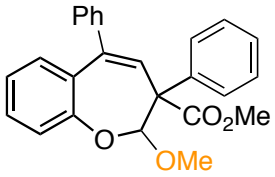

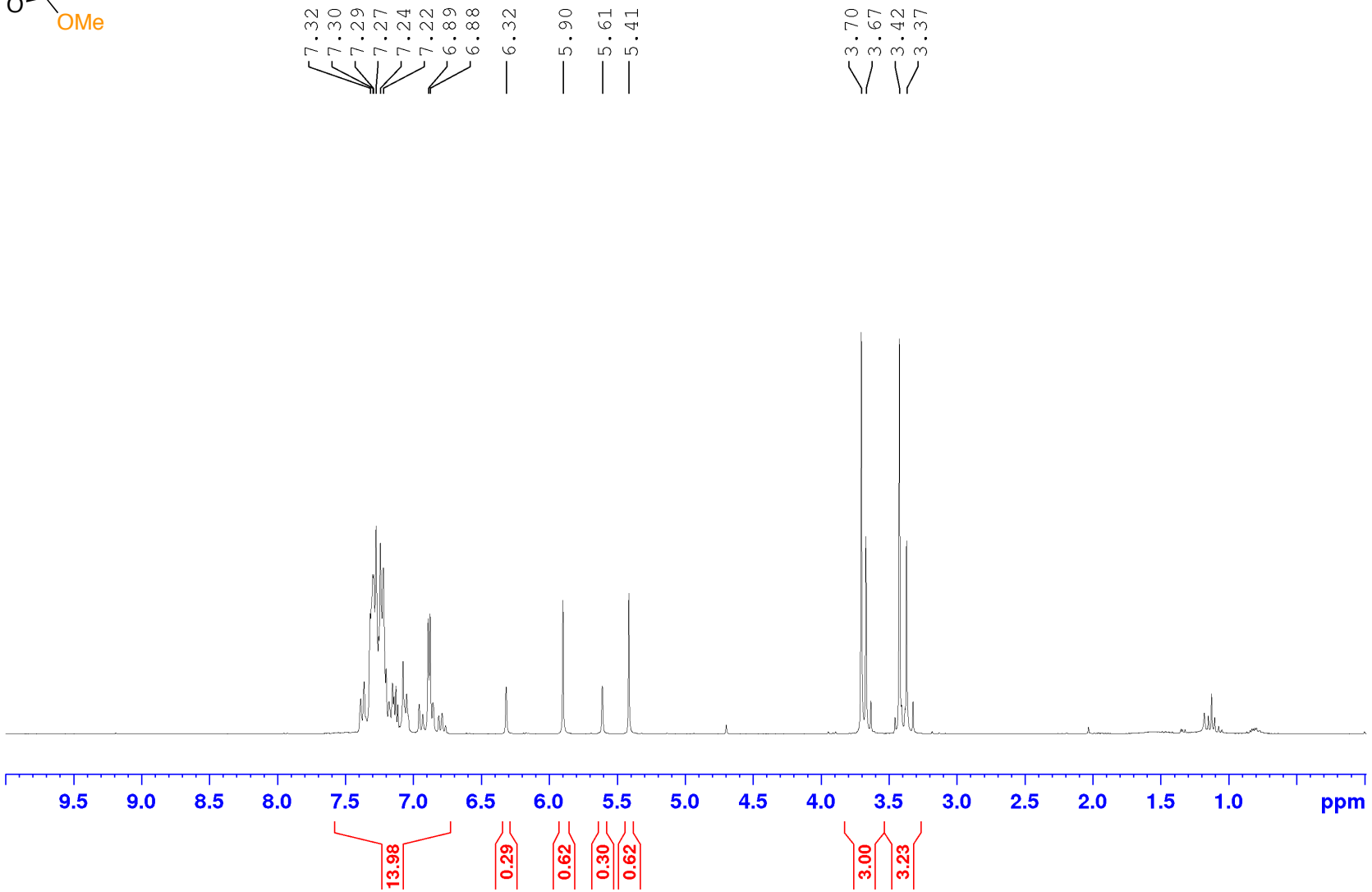

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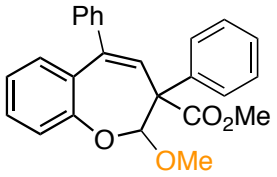

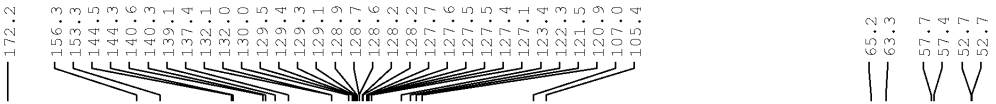

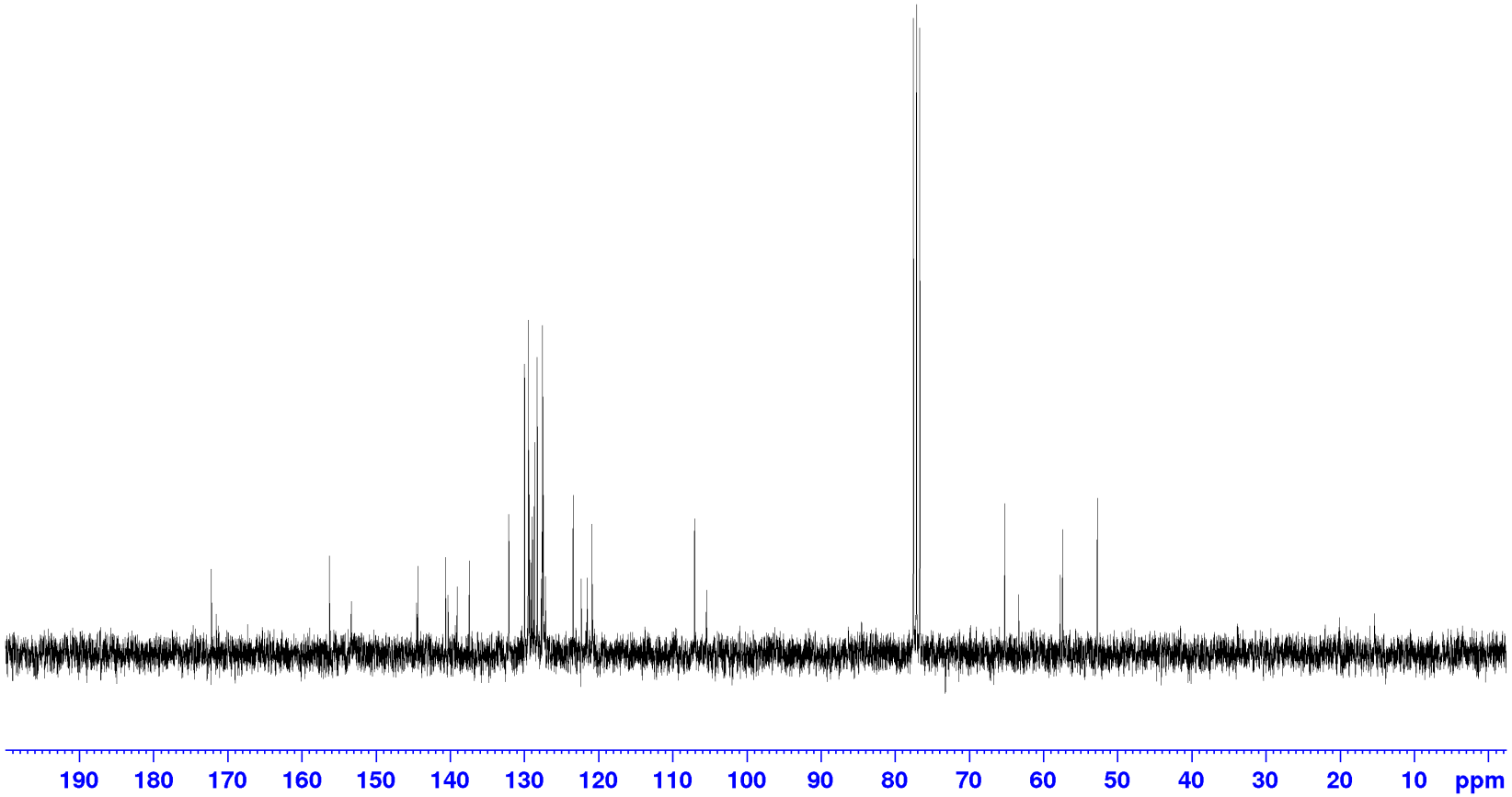

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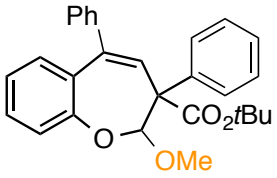
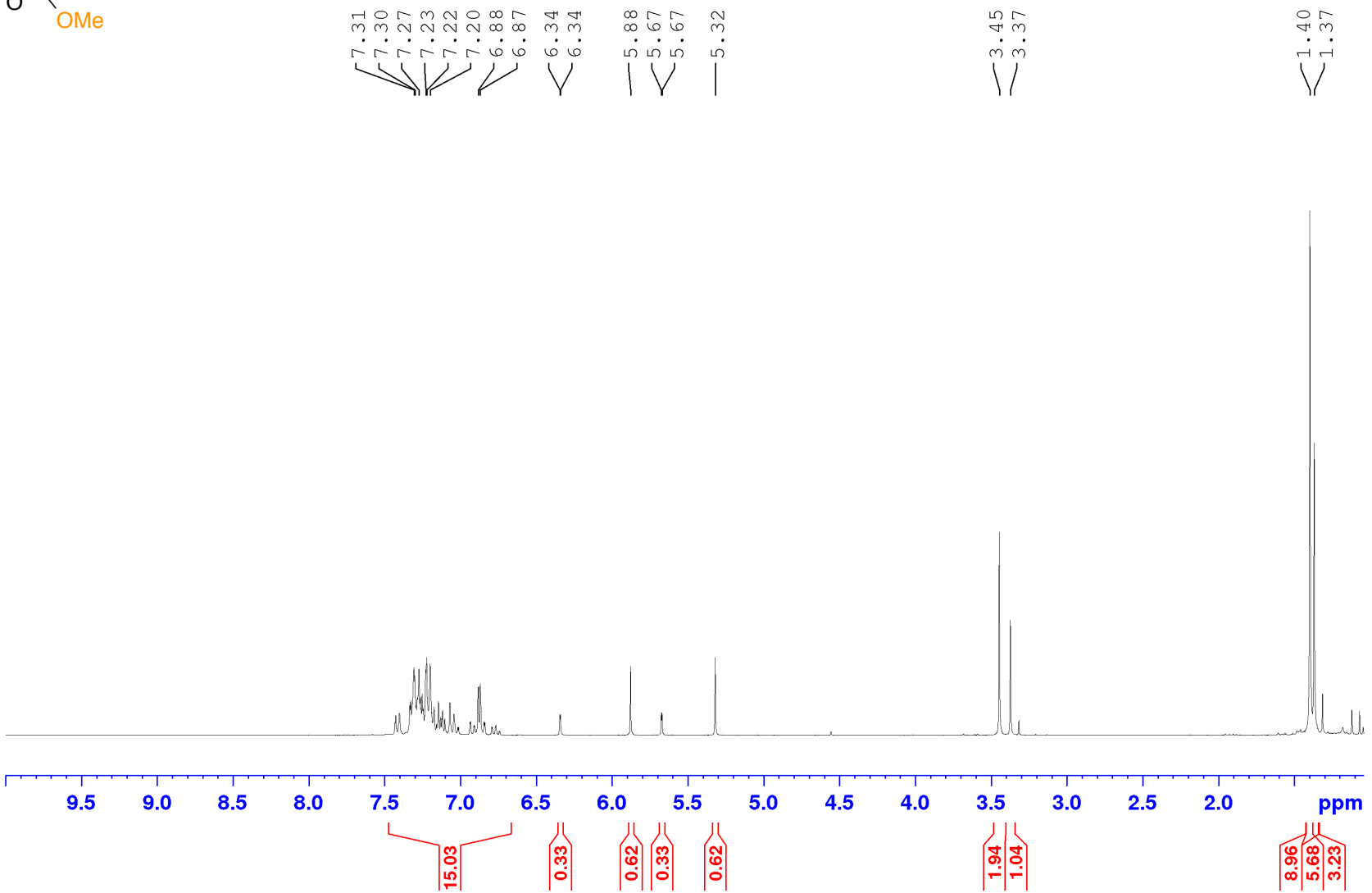
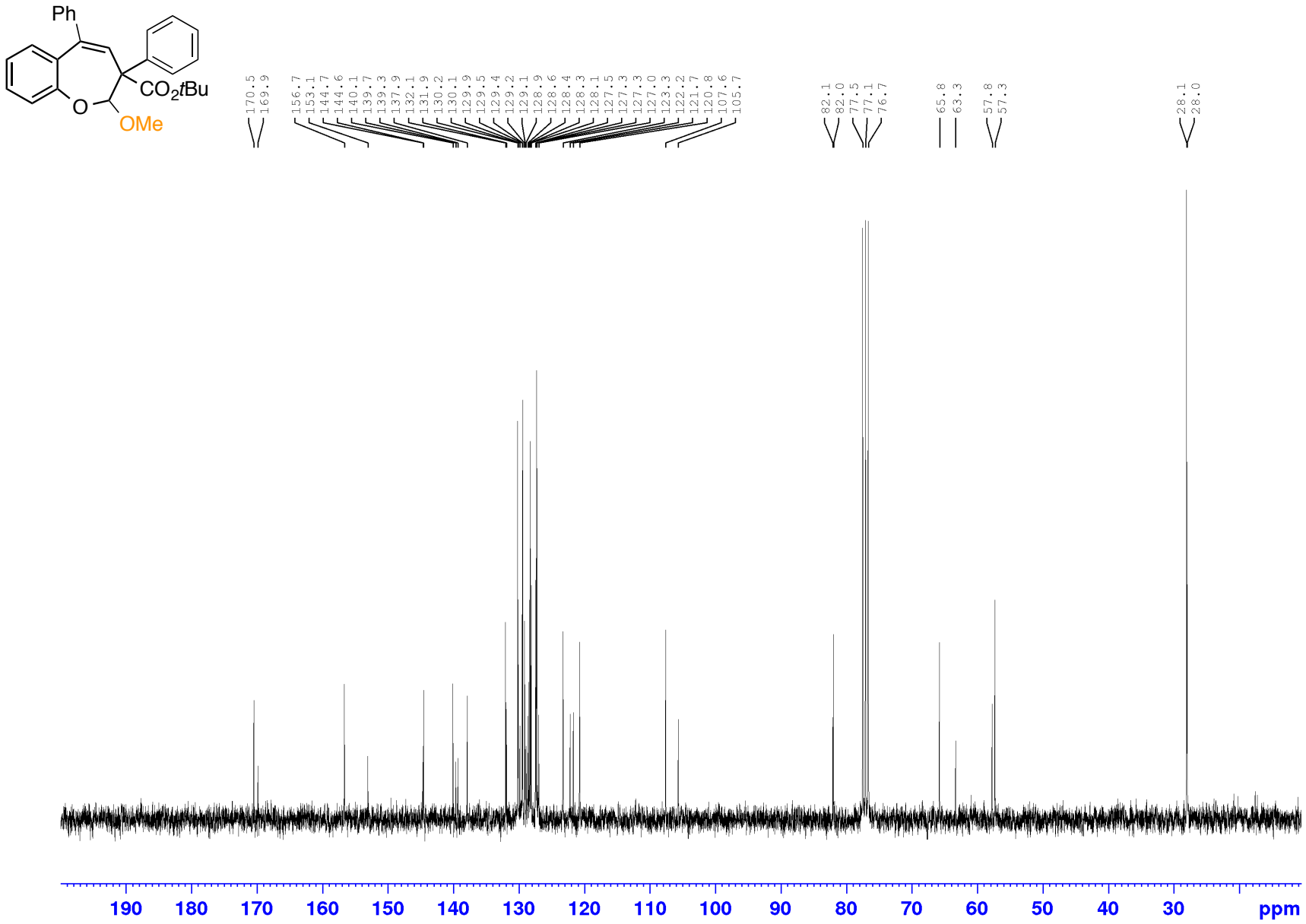




tert-butyl 2-methoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate 5



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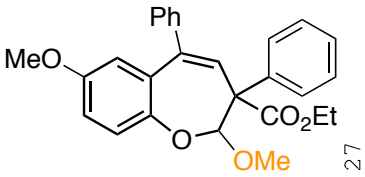

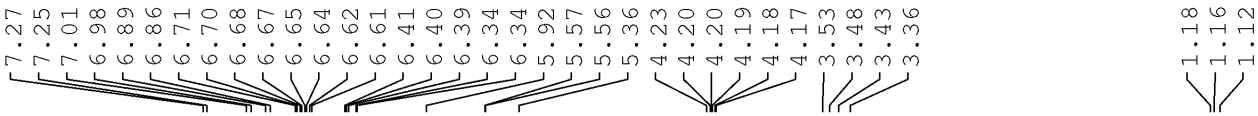

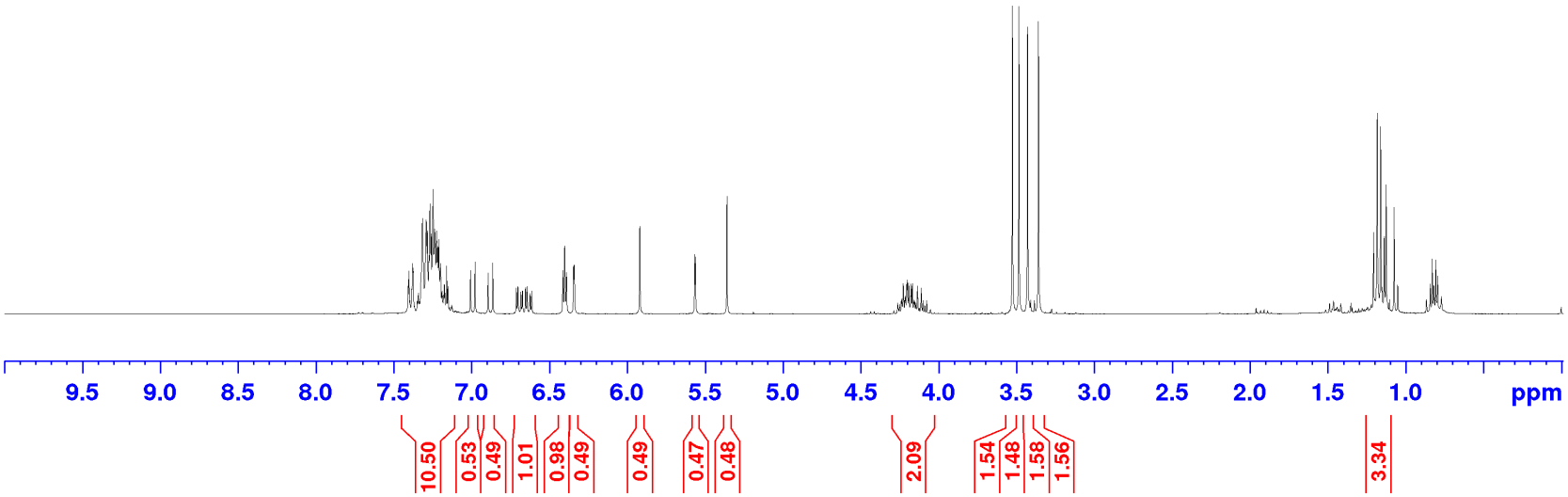

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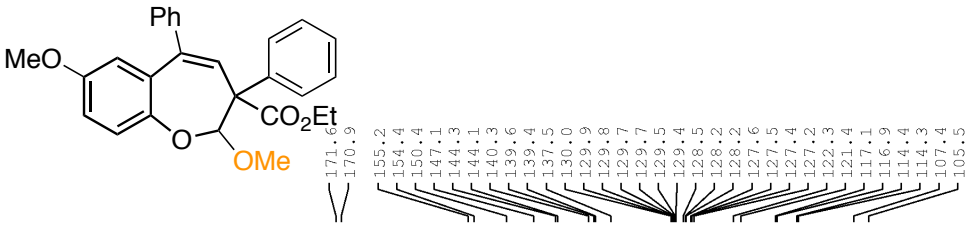

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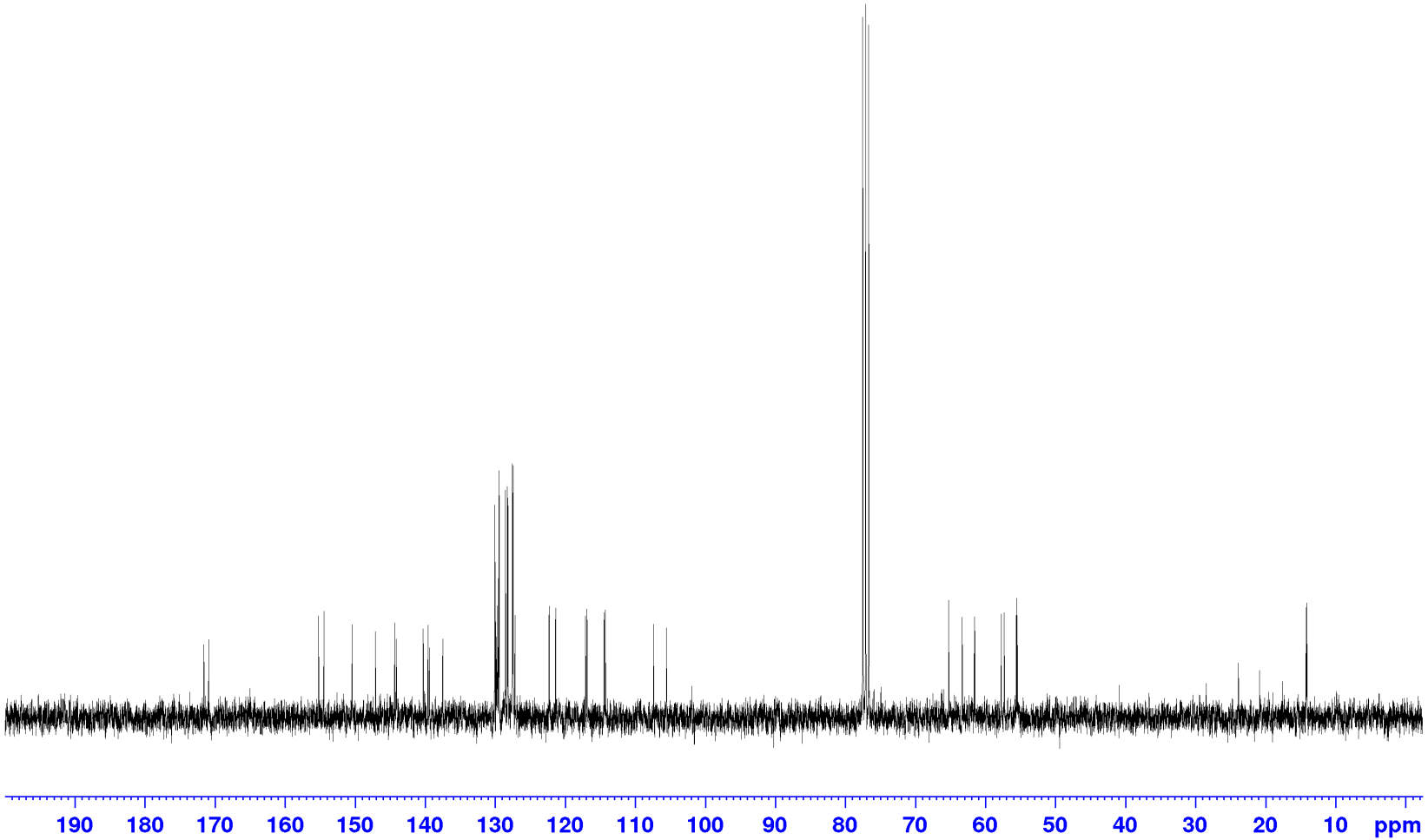
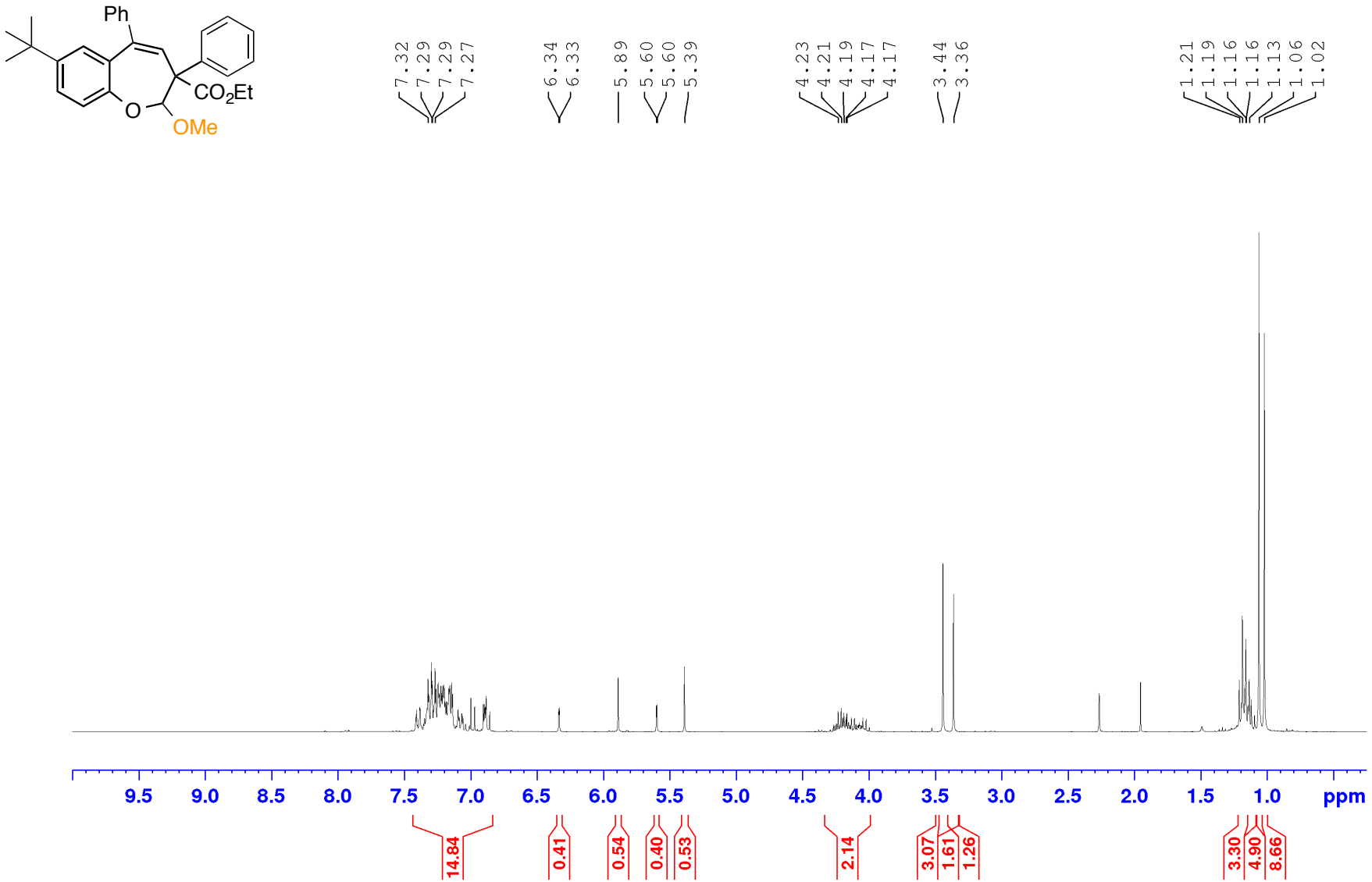
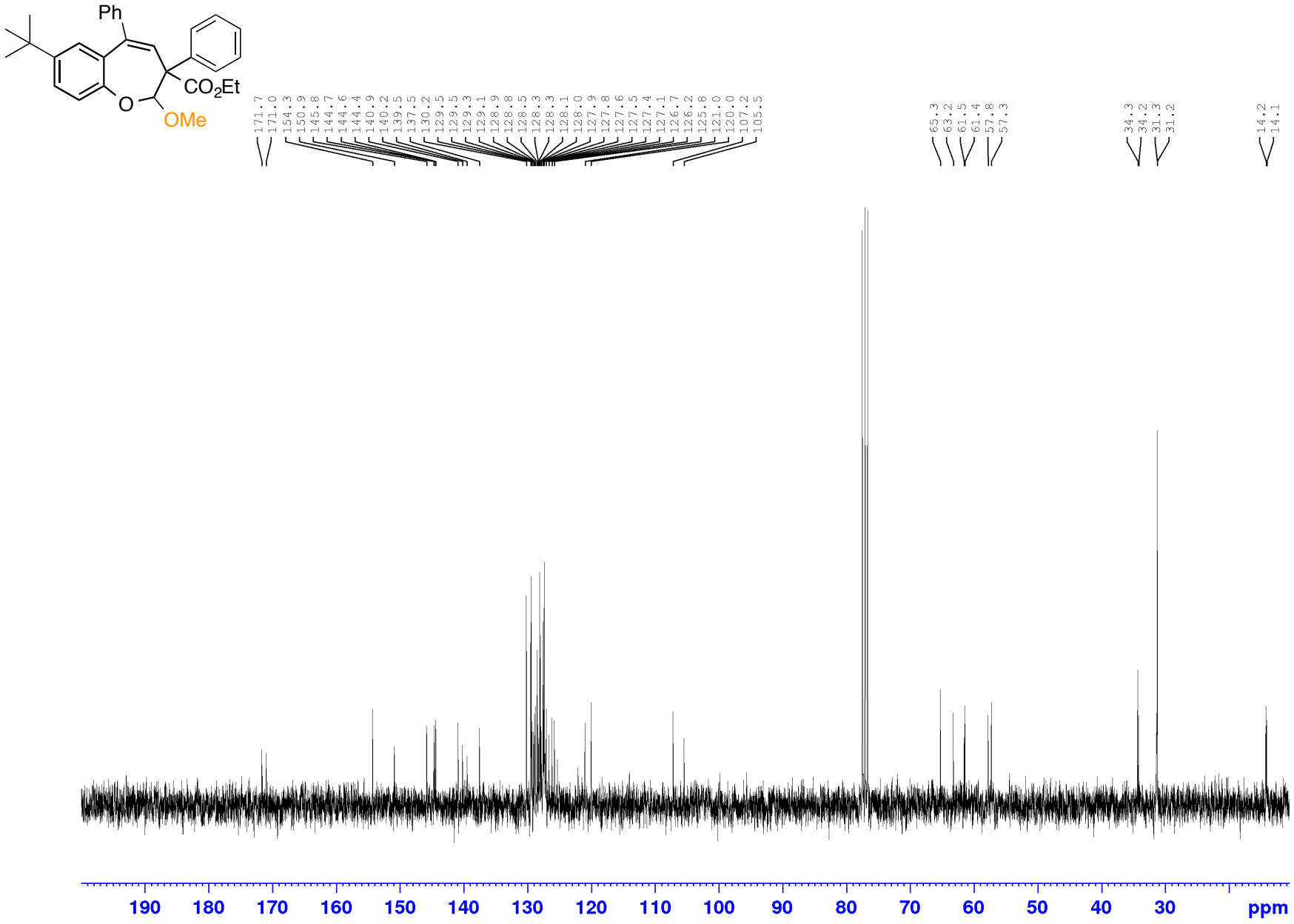


ethyl 7-(tert-butyl)-2-methoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate ***7***



ethyl 7-(tert-butyl)-2-methoxy-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate ***7***



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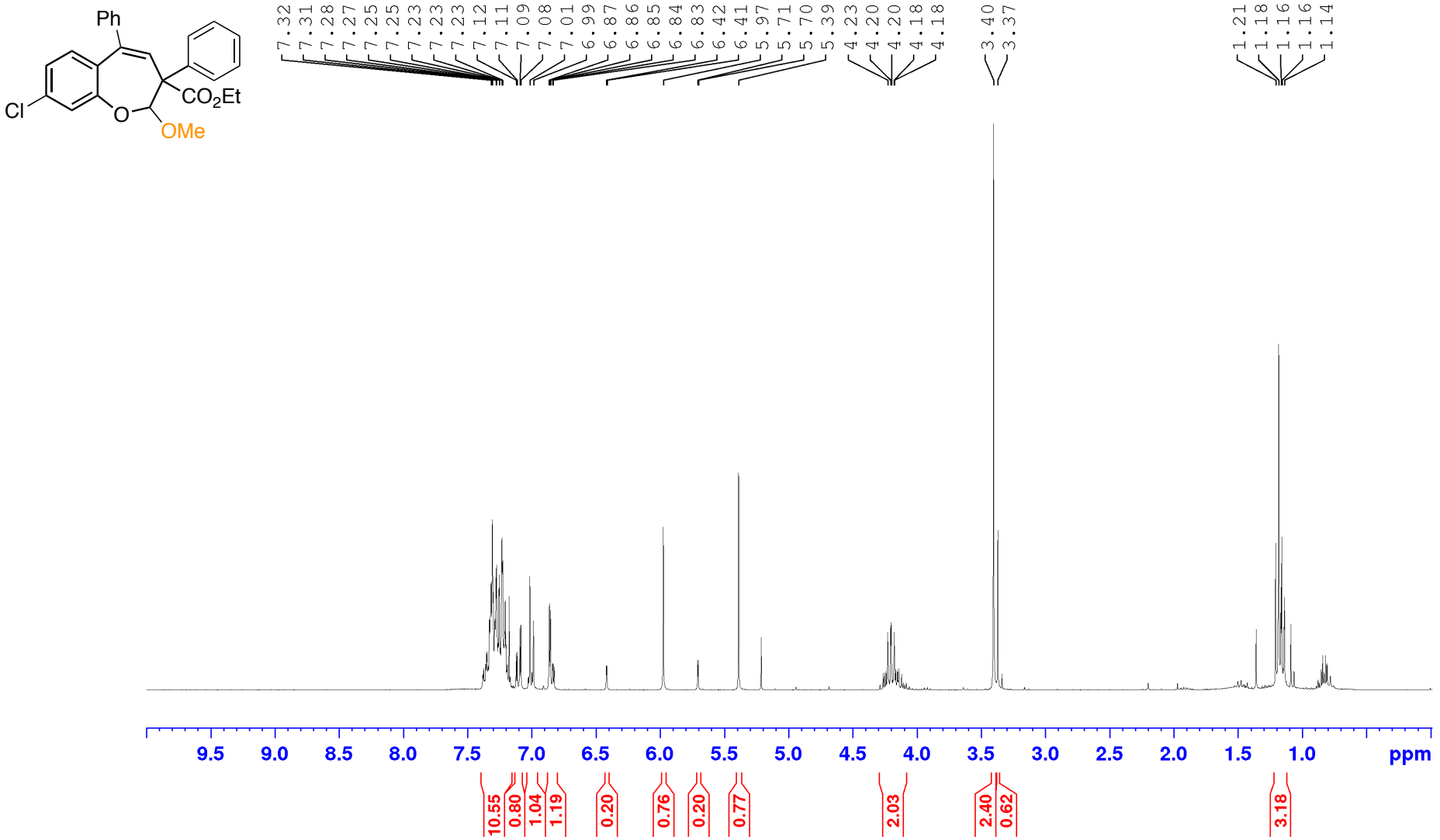

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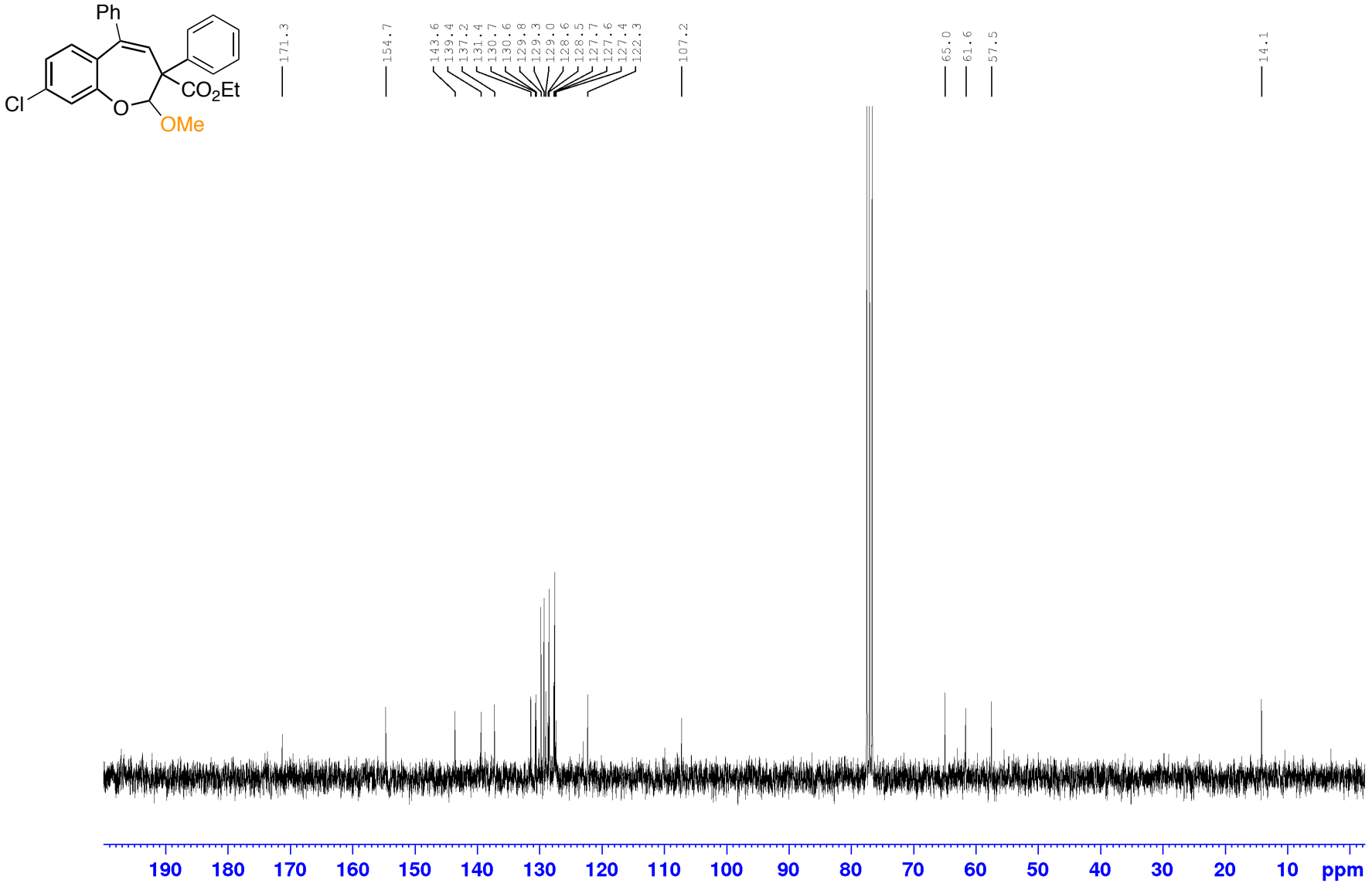

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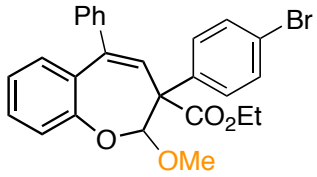

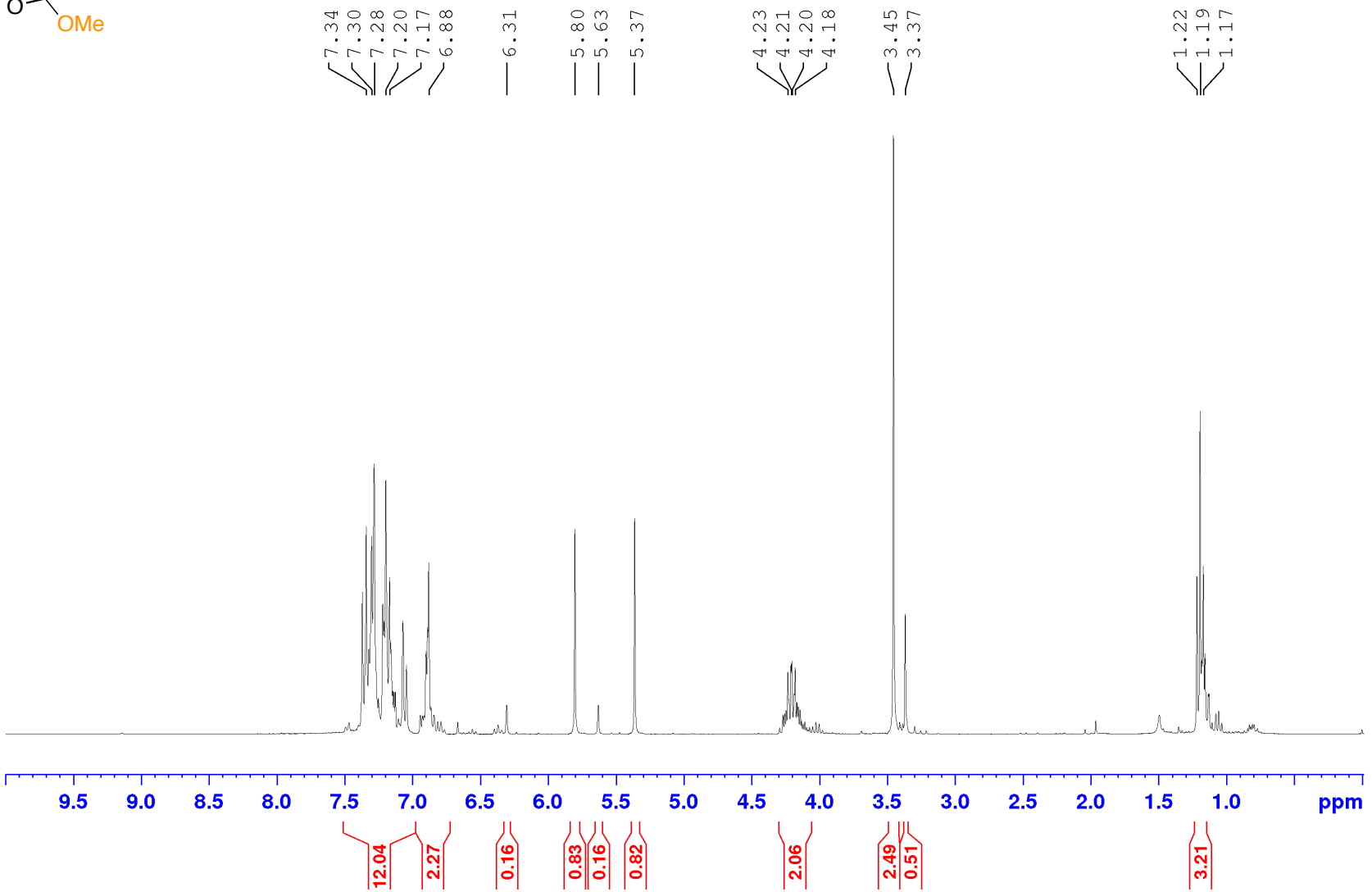

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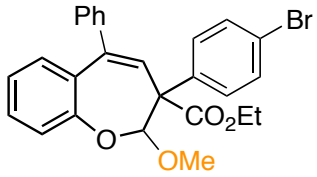

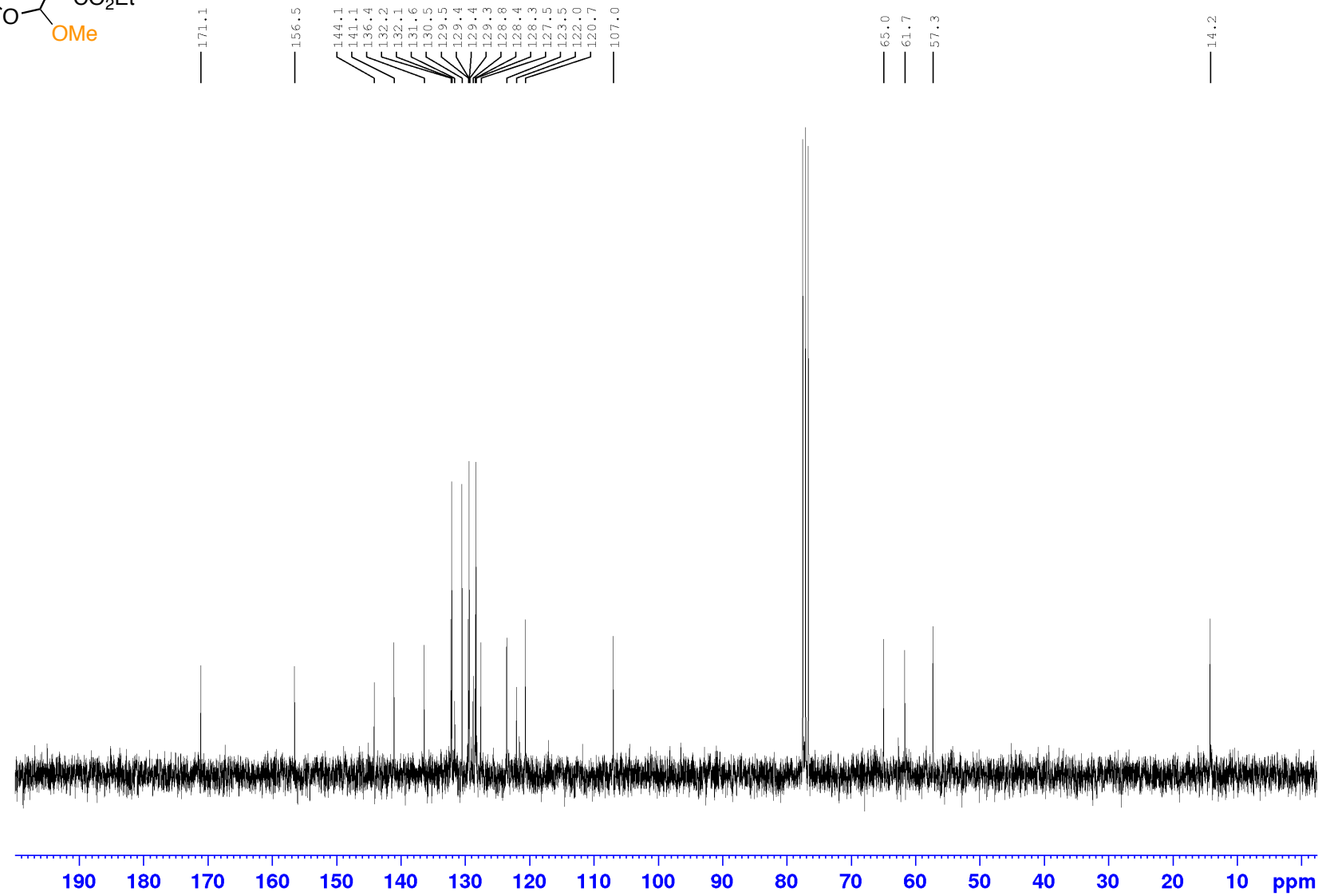

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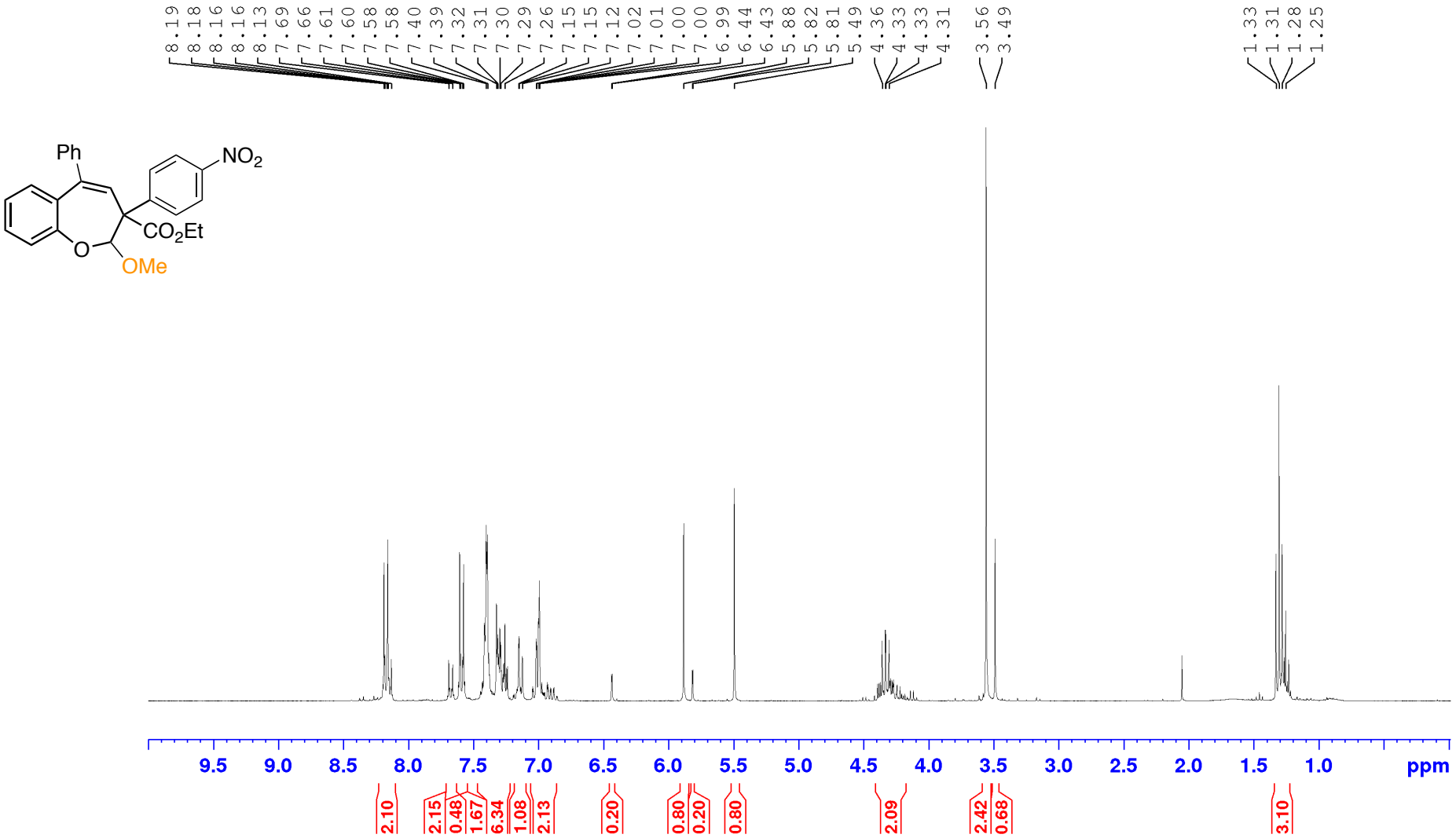

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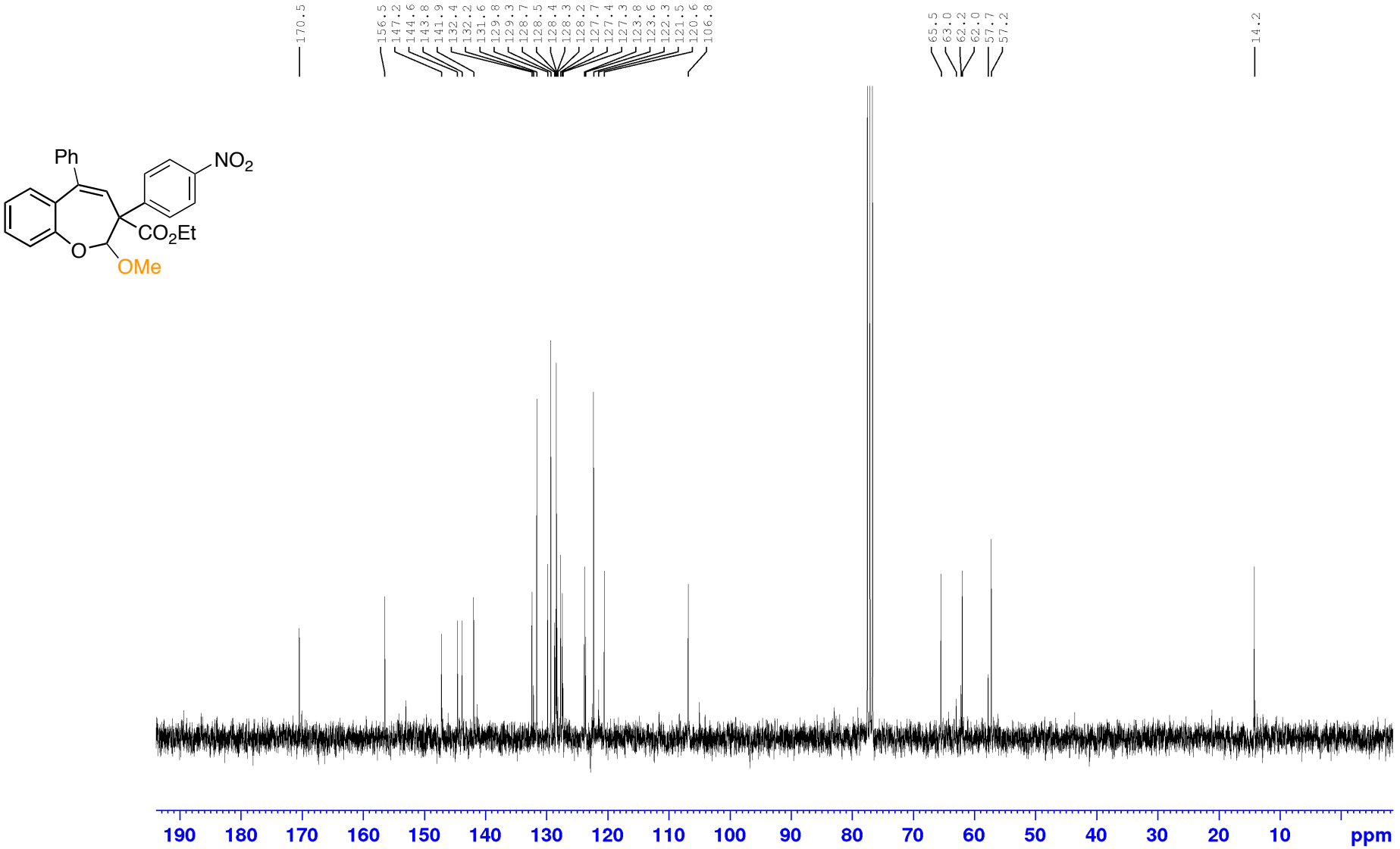
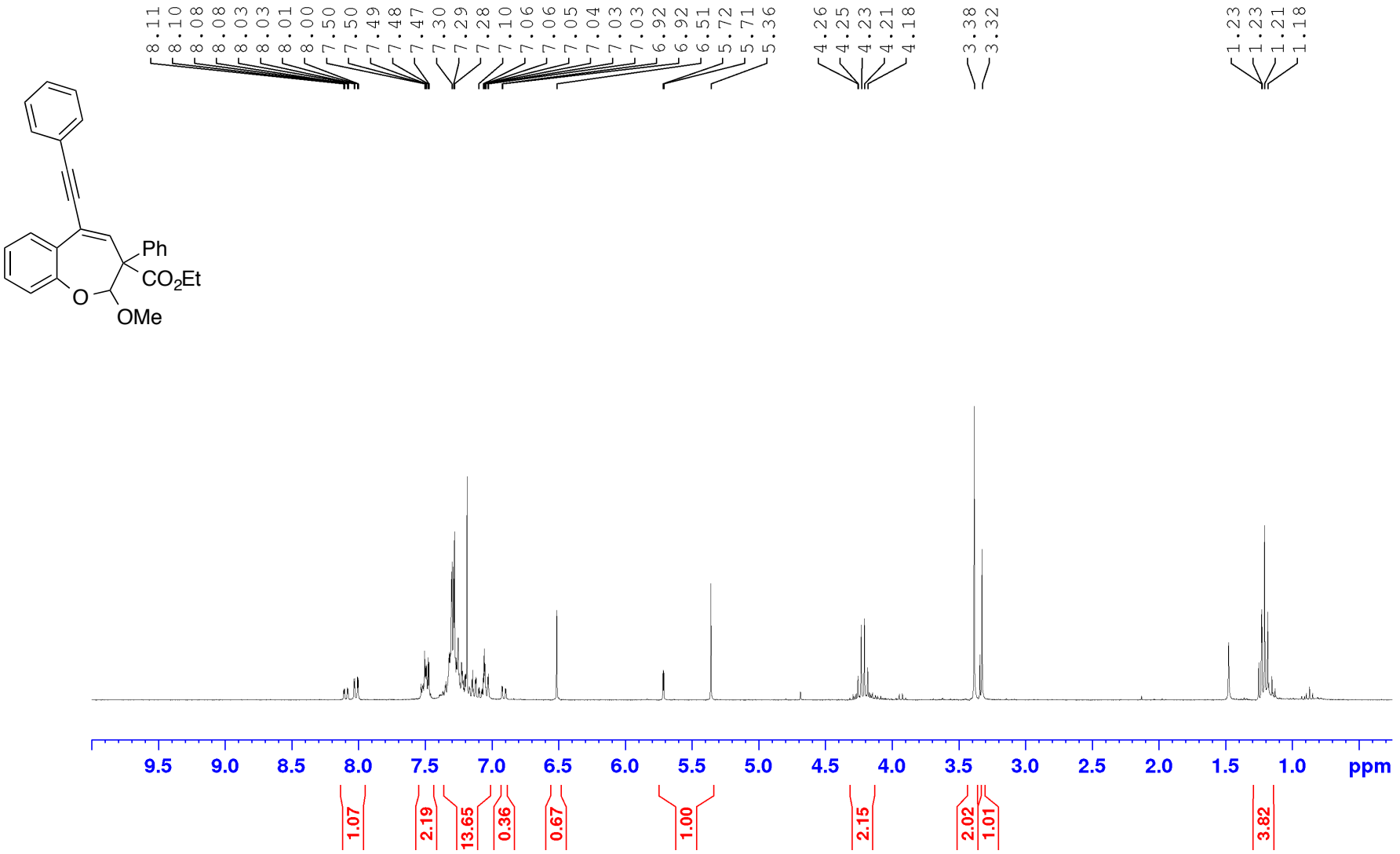
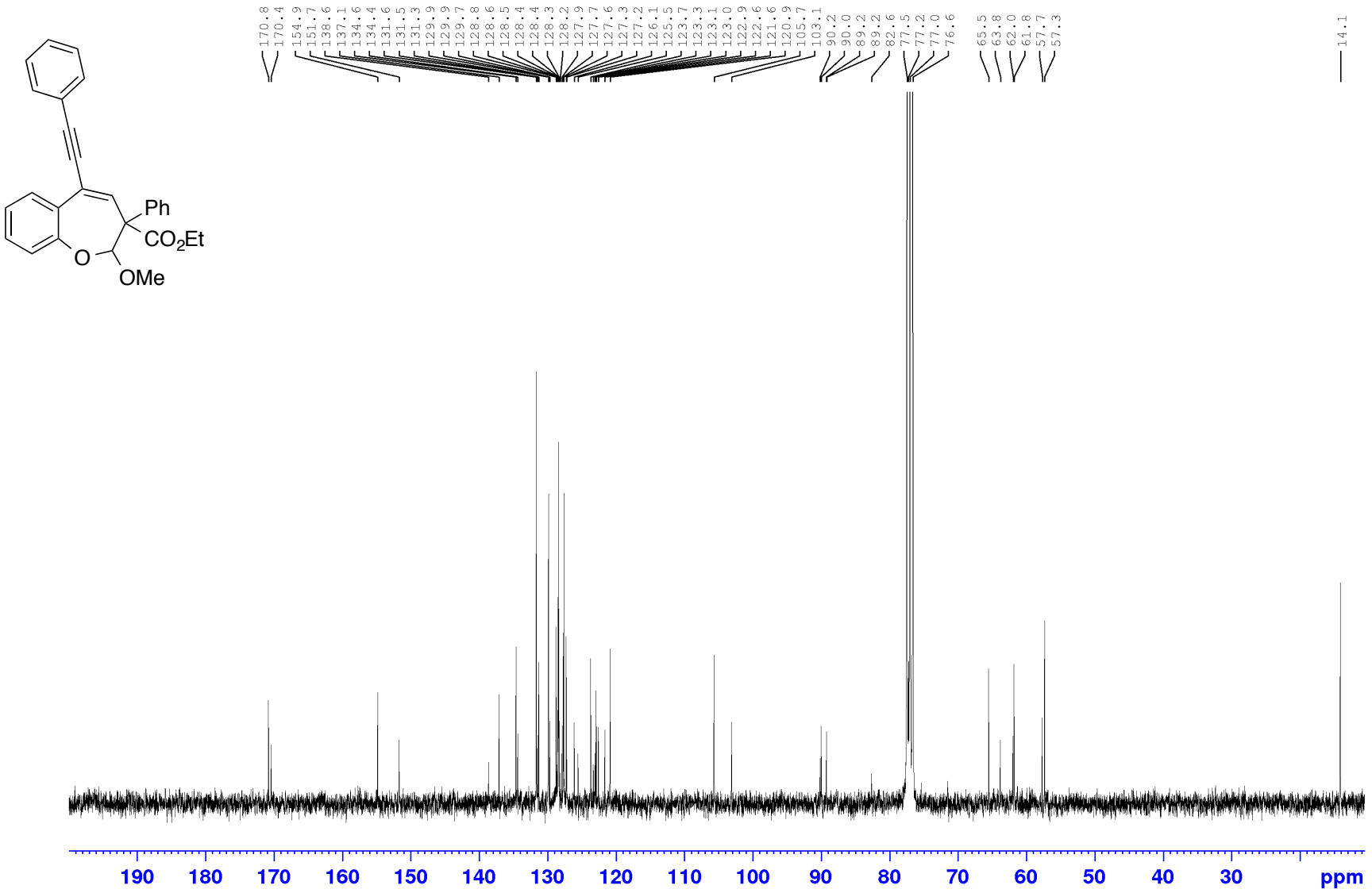


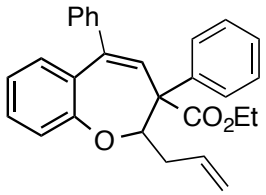
ethyl 2-methoxy-3-phenyl-5-(phenylethynyl)-2,3-dihydrobenzo[b]oxepine-3-carboxylate ***11***

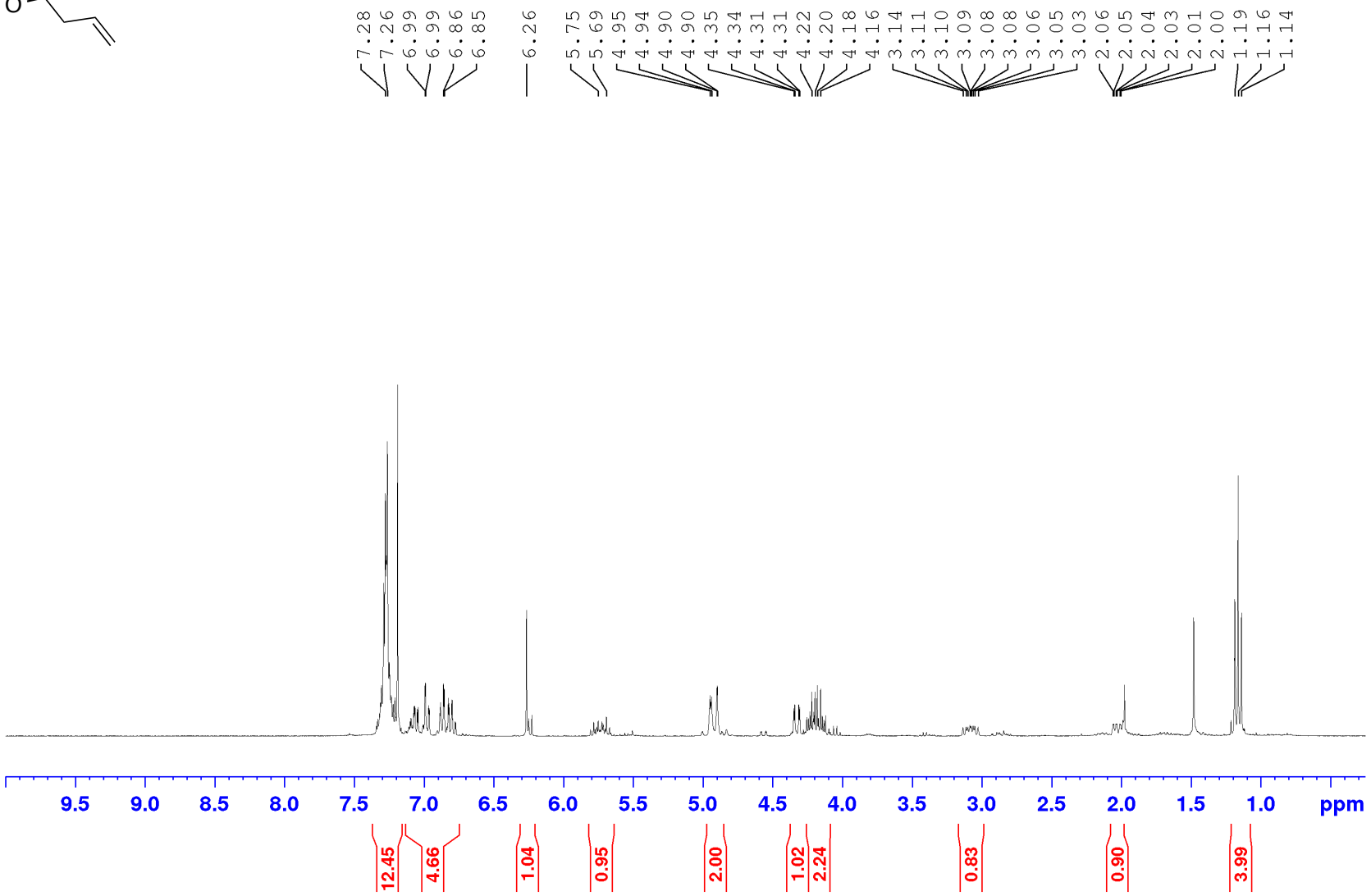


ethyl 2-methoxy-3-phenyl-5-(phenylethynyl)-2,3-dihydrobenzo[b]oxepine-3-carboxylate ***11***



ethyl 2-allyl-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate ***12***





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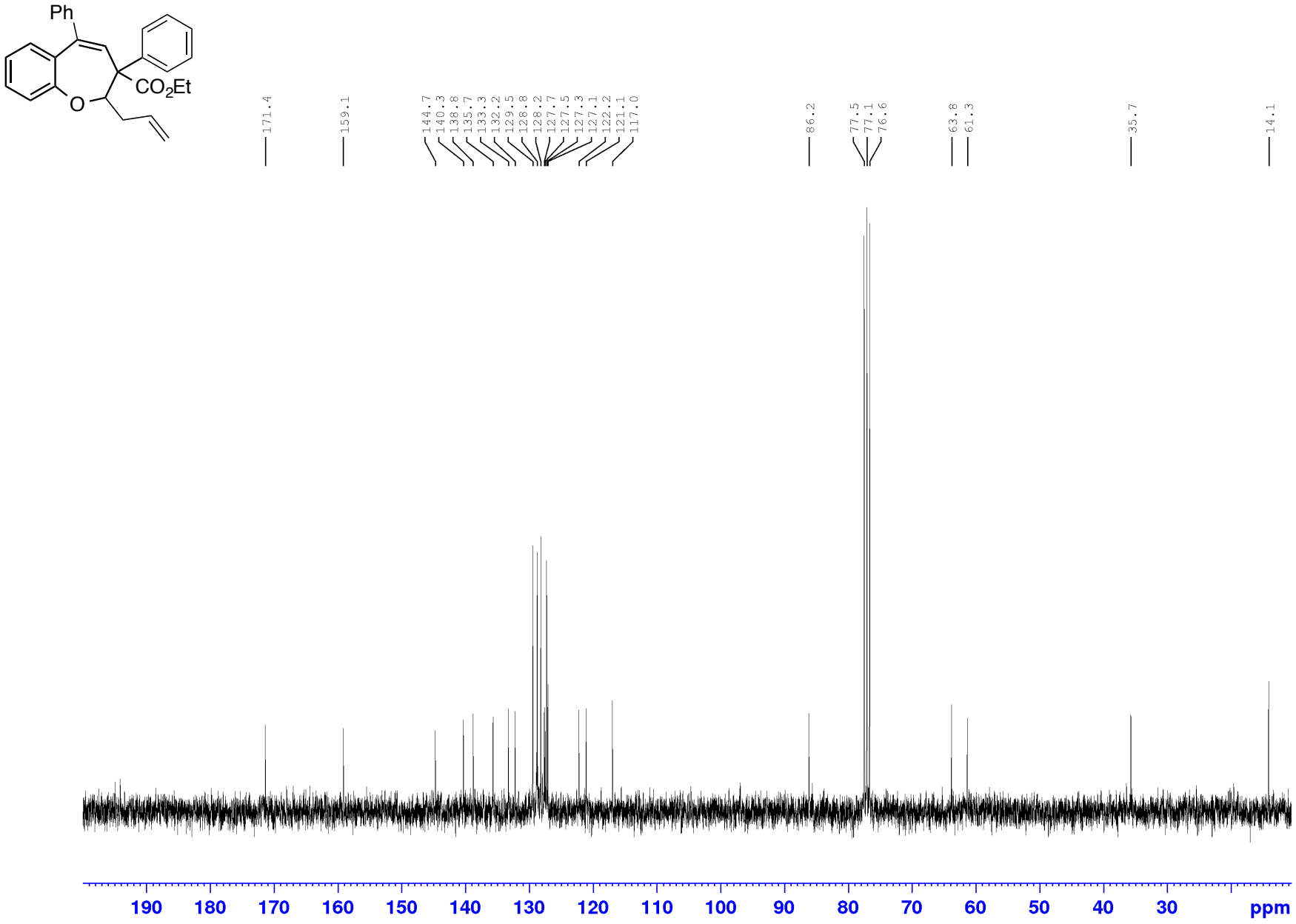
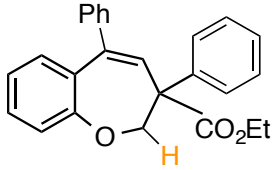
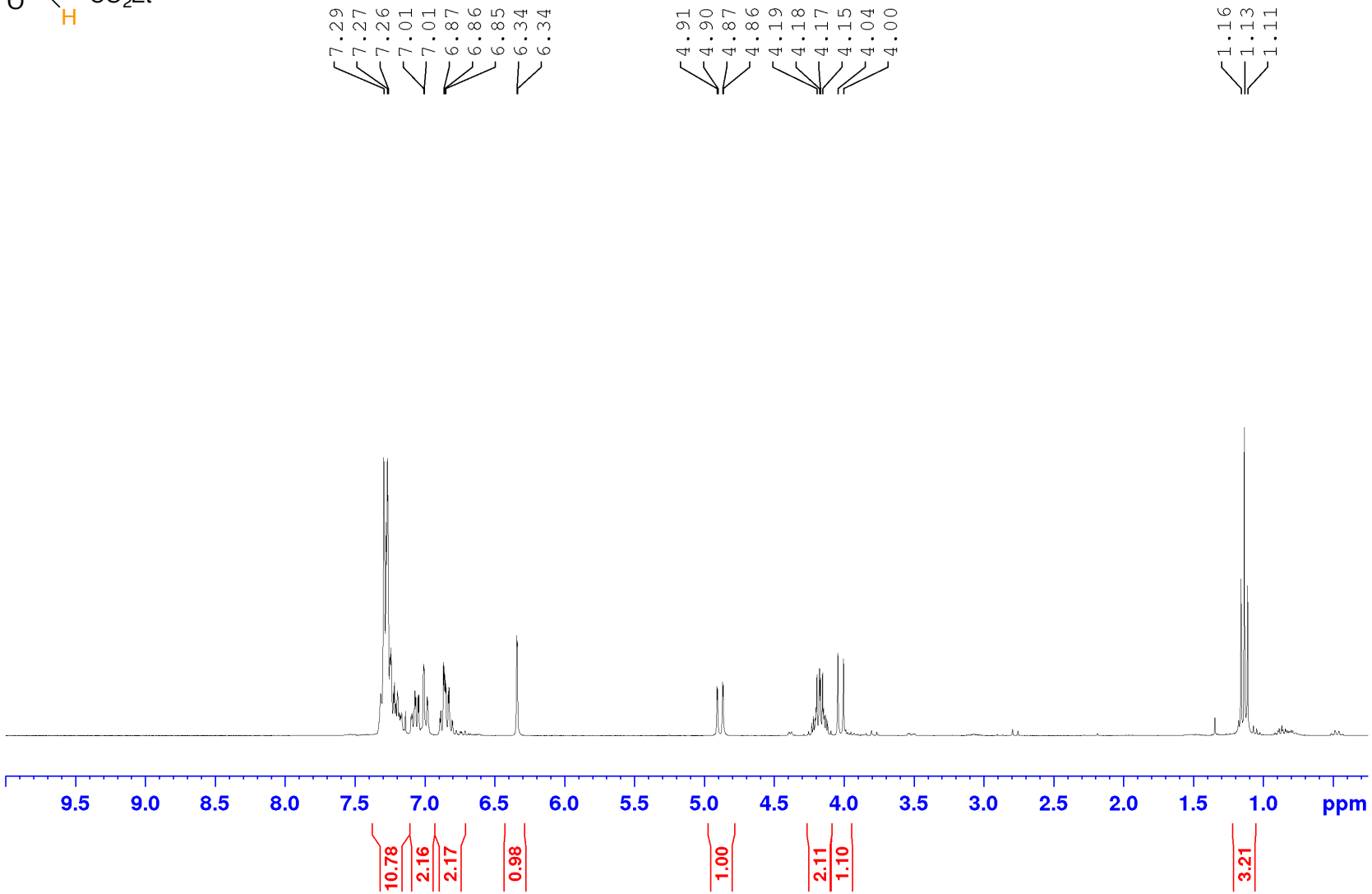
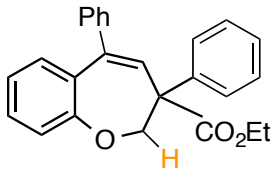


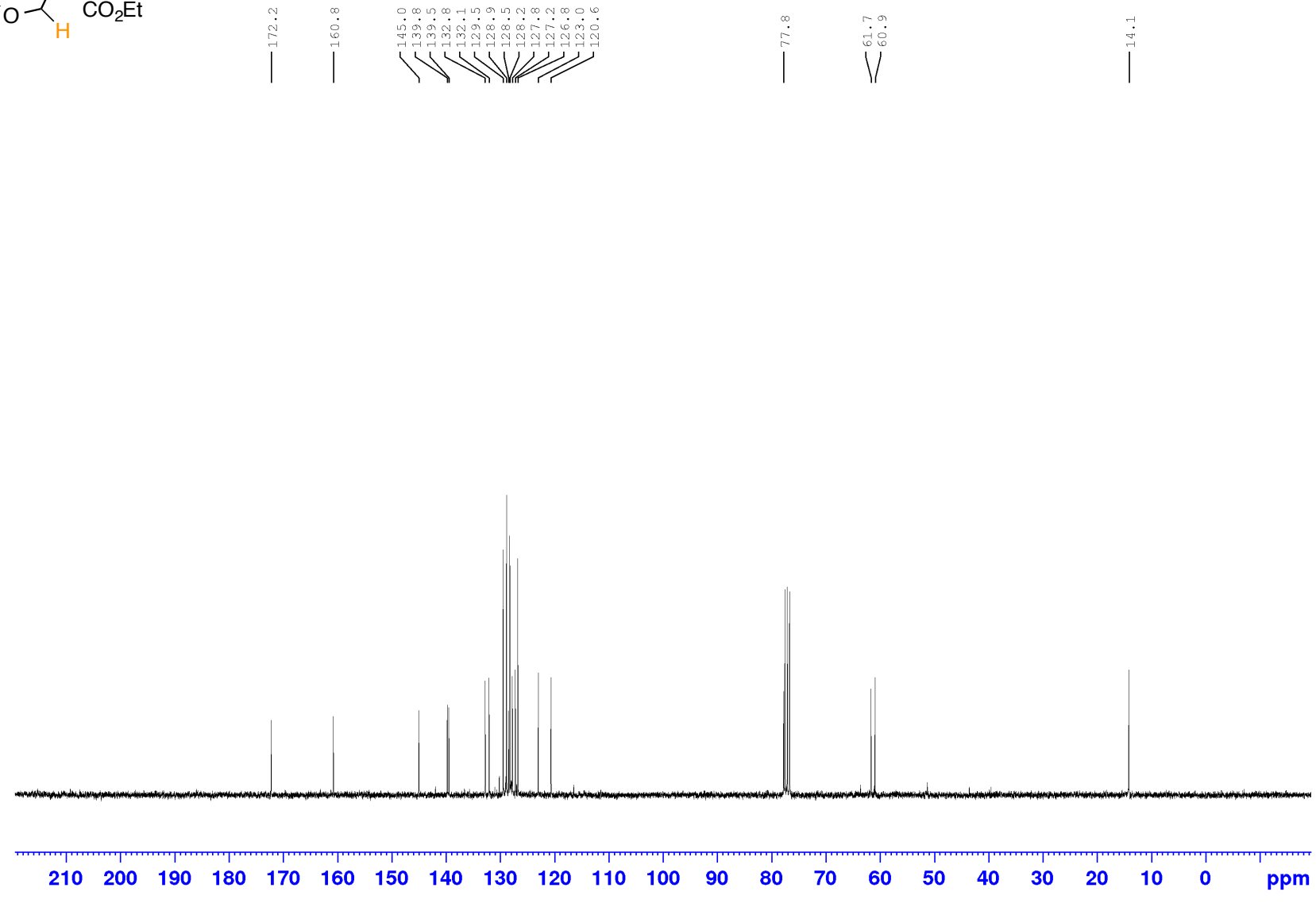
3,5-diphenyl-2,3-dihydrobenzo[b]oxepin-3-yl propionate ***13***



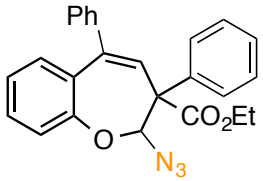


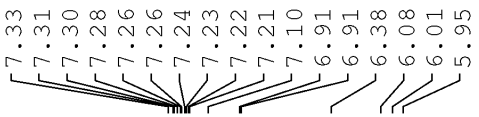
3,5-diphenyl-2,3-dihydrobenzo[b]oxepin-3-yl propionate ***13***

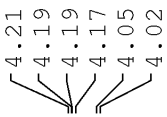


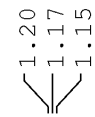


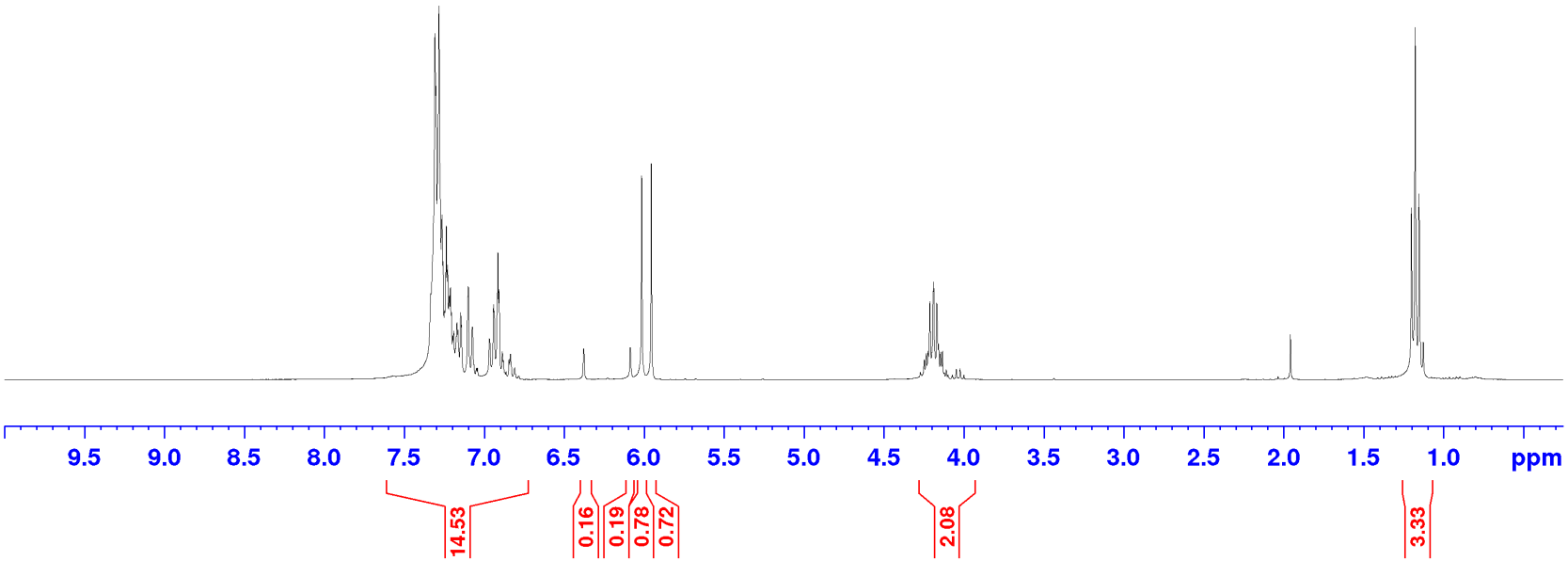
ethyl 2-azido-3,5-diphenyl-2,3-dihydrobenzo[b]oxepine-3-carboxylate 14











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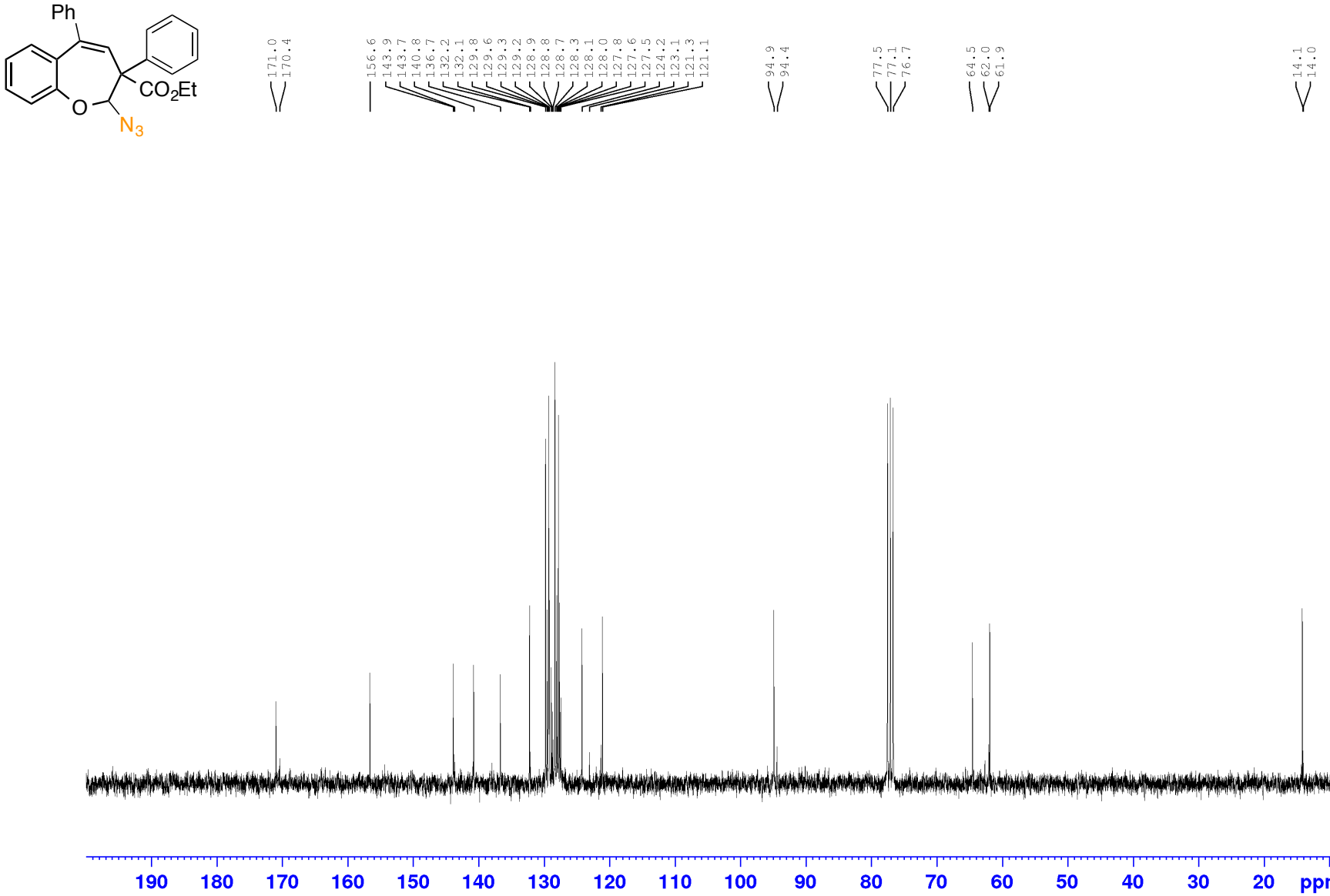

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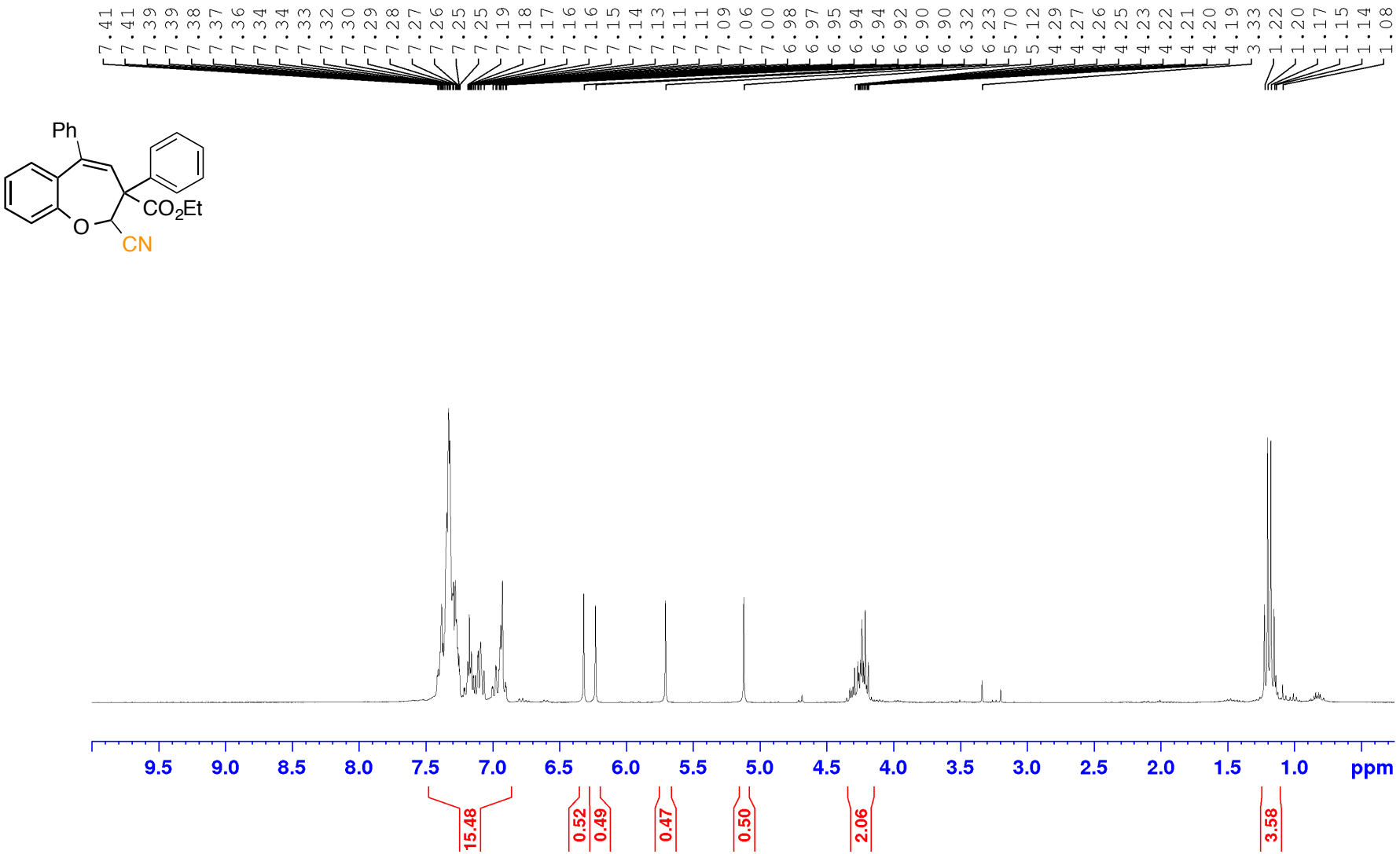

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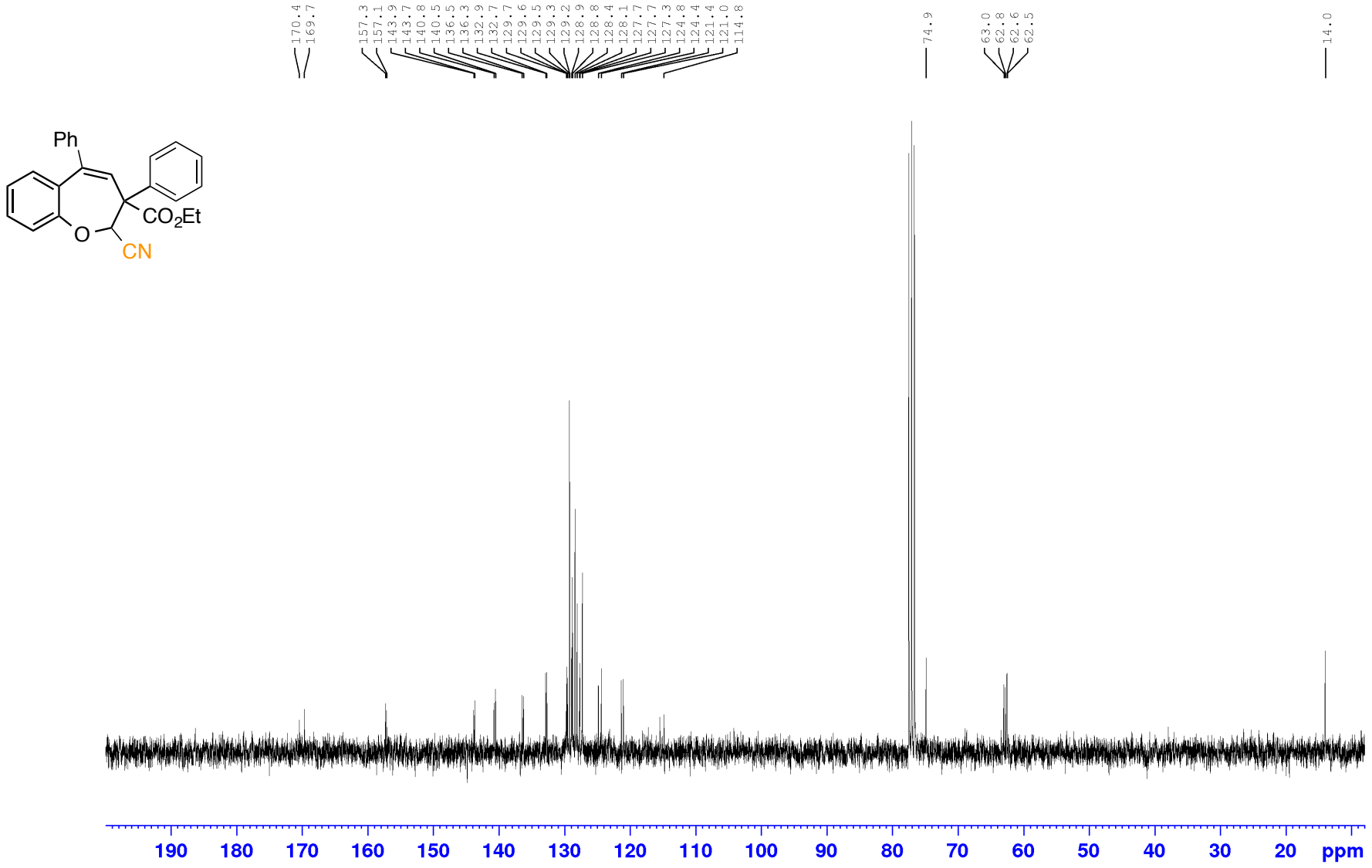

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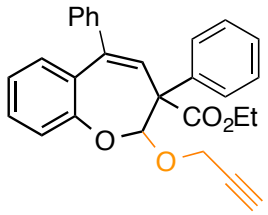
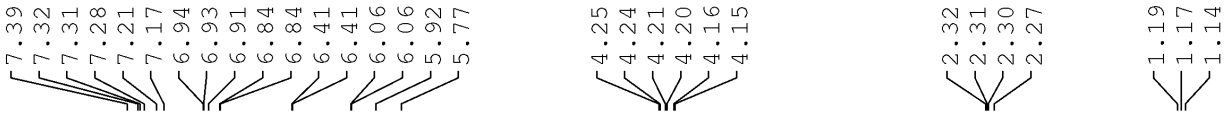
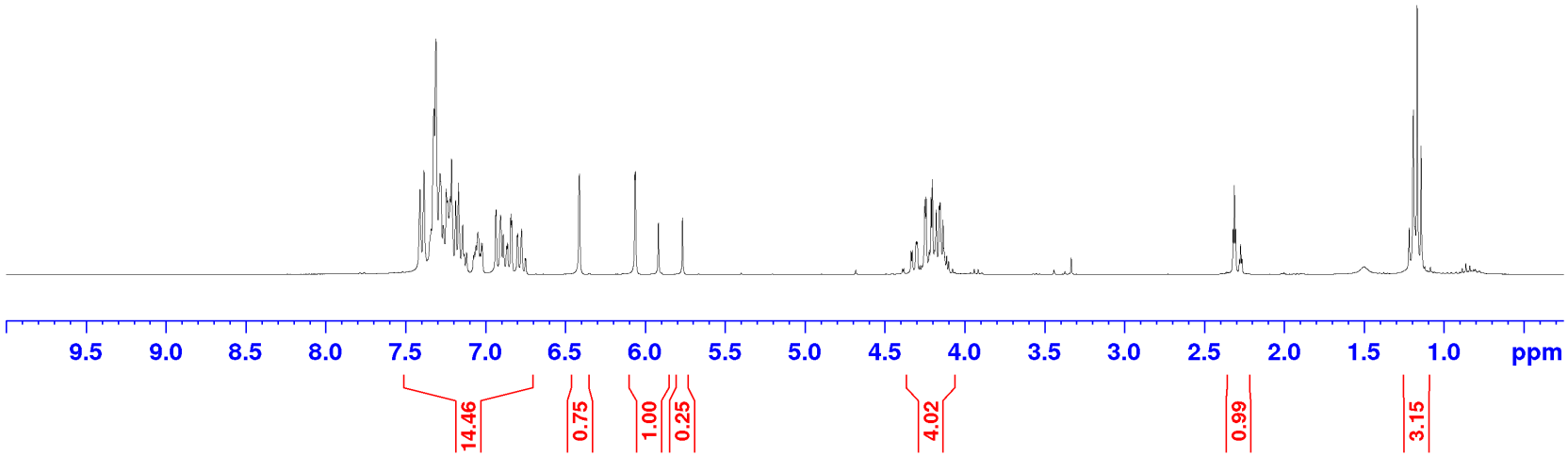
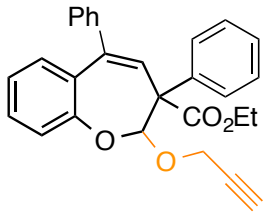






ethyl 3,5-diphenyl-2-(prop-2-yn-1-yloxy)-2,3-dihydrobenzo[b]oxepine-3-carboxylate 16



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