

# SUPPORTING INFORMATION

## Structure and Reactivity of Half-Sandwich Rh(+3) and Ir(+3) Carbene Complexes. Catalytic Metathesis of Azobenzene Derivatives

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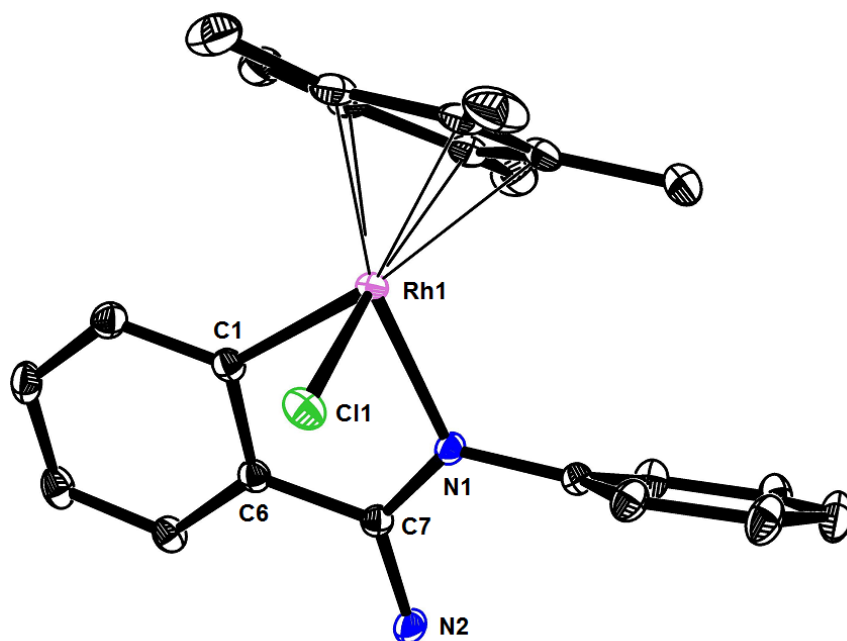
### *Table of Contents*

Additional Crystallographic Information	S2
General	S3
Substrates	S4
Structural and Mechanistic Investigations	S5
Substrate and Catalyst Screening	S9
Metathesis of Azobenzene Derivatives	S12
Stoichiometric Low Temperature NMR Experiments for the Characterization of the Diaziridine Intermediate	S19
Spectra	S22

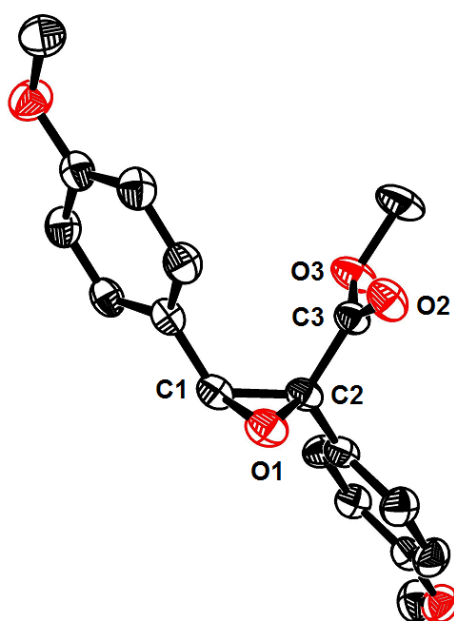
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## ADDITIONAL CRYSTALLOGRAPHIC INFORMATION

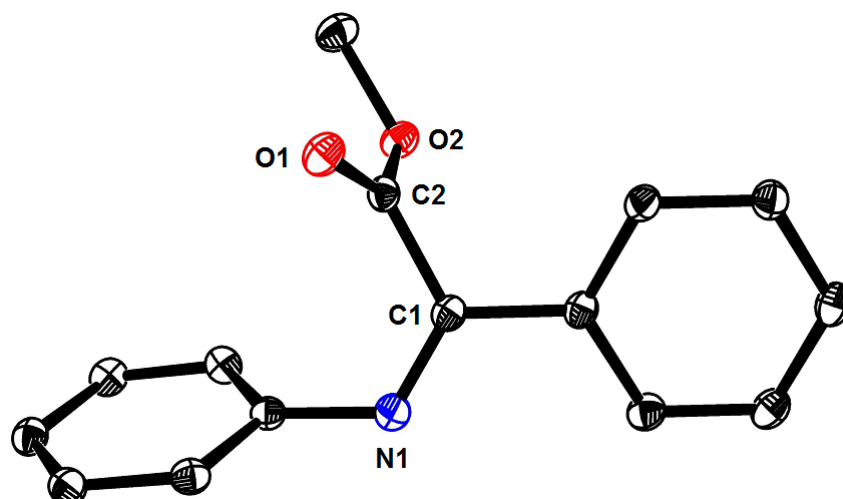
CCDC 1575834 (**3**), 1443595 (**12**), 1575835 (**13**), 1575836 (**14a**), 1575837 (**15**) and 1575838 (**41**) contain the crystallographic data of the complexes shown in the paper; CCDC 1575459 (**4**), 1575460 (**8**) and 1575461 (**17**) contain the crystallographic data of the complexes shown below (SI only):



**Figure S1.** Structure of the cyclometalated complex **4** in the solid state



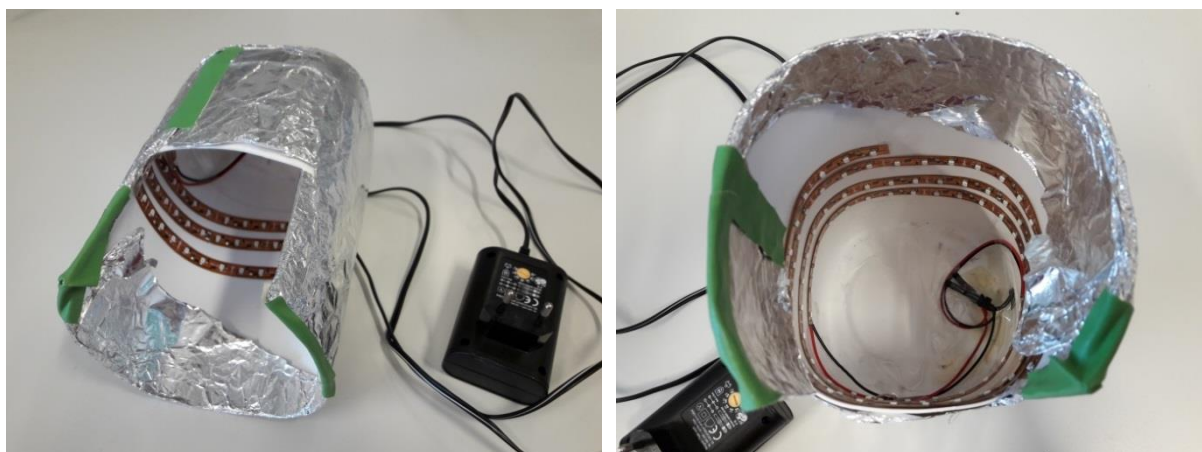
**Figure S2.** Structure of epoxide **8** (X = OMe, R = MeOC<sub>6</sub>H<sub>4</sub>-) in the solid state



**Figure S3.** Structure of imine **17** formed by azobenzene metathesis

**General.** All reactions were carried out under an Ar atmosphere in flame-dried glassware unless stated otherwise. Solvents were purified by distillation over the indicated drying agents and were transferred under Ar: toluene (Na/K, stored over molecular sieves), 1,2-dichloroethane (CaH<sub>2</sub>), CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>), CD<sub>2</sub>Cl<sub>2</sub> (dried and stored over molecular sieves, degassed three times by the freeze-pump-thaw method), methanol (Mg), pentane (Na/K, degassed three times by the freeze-pump-thaw method), fluorobenzene (CaH<sub>2</sub>); pyridine was dried by an absorption solvent purification system based on molecular sieves. Flash chromatography: Merck Geduran<sup>®</sup> Si 60 (40–63 μm). NMR: Spectra were recorded at room temperature unless stated otherwise, on Bruker AV 400s and AV 500as spectrometers in the indicated solvents; chemical shifts ( $\delta$ ) are given in ppm relative to TMS (<sup>15</sup>N spectra were referenced externally to MeNO<sub>2</sub>), coupling constants ( $J$ ) in Hz. The solvent signals were used as references (CDCl<sub>3</sub>:  $\delta_c$  = 77.16 ppm; residual CHCl<sub>3</sub> in CDCl<sub>3</sub>:  $\delta_H$  = 7.26 ppm; CD<sub>2</sub>Cl<sub>2</sub>:  $\delta_c$  = 53.84 ppm; residual CHDCl<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub>:  $\delta_H$  = 5.32 ppm); <sup>1</sup>H and <sup>13</sup>C assignments were established using NOESY, HSQC and HMBC experiments; numbering schemes as shown in the Inserts. IR: Perkin-Elmer Spectrum One spectrometer, wavenumbers ( $\tilde{\nu}$ ) in cm<sup>-1</sup>. MS: EI: Finnigan MAT 8400 (70 eV), ESI: Thermo Scientific LTQ-FT or Thermo Scientific Exactive, GC-EI: Thermo Scientific Trace GC Ultra with a Thermo Scientific ISQ spectrometer, accurate mass determinations: Finnigan MAT 95, Thermo Scientific LTQ FT, or Thermo Scientific Exactive.

A self-made set-up was used for reactions carried out under irradiation with light emitted by blue LEDs. Two LED strips were secured to the inside of a plastic container (12 cm×12 cm×18 cm), of which the end was cut open (Figure S4). The LED strips were purchased from Conrad Electronic SE ([www.conrad.de](http://www.conrad.de), SKU: 150536) and possess the following characteristics: wave length  $\lambda$  = 470 nm, luminous intensity  $I_v$  = 250 mcd, angle of radiation 110°, 48 LEDs per strip (3 per unit), strip length 67.2 cm, 12 V, 5.2 W.

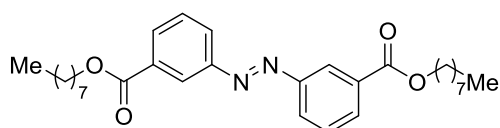


**Figure S4:** Self-made LED array.

**Substrates.** Unless stated otherwise, all commercially available compounds (ABCR, Acros, Sigma-Aldrich, TCI) were used as received.  $[\text{Cp}^*\text{RhCl}_2]_2$  and  $[\text{Cp}^*\text{Rh}(\text{MeCN})_3](\text{SbF}_6)_2$  were purchased from STREM.  $[\text{Cp}^*\text{IrCl}_2]_2$ ,  $[\text{Cp}^*\text{IrI}_2]_2$  and  $[\text{IrCl}(\text{cod})]_2$  were purchased from Sigma-Aldrich and used as received.

The following compounds were prepared according to the cited literature:  $[\text{Cp}^*\text{RhI}_2]_2$ ,<sup>1</sup>  $[\text{Cp}^*\text{RhBr}_2]_2$ ,<sup>2</sup> bis(4-methoxyphenyl)diazomethane (**5a**),<sup>3</sup> bis(4-(dimethylamino)phenyl)diazomethane (**5b**),<sup>4</sup> methyl 2-diazo-2-(4-methoxyphenyl)acetate (**6a**),<sup>5</sup> methyl 2-diazo-2-phenylacetate (**6b**),<sup>5</sup> methyl 4-(1-diazo-2-ethoxy-2-oxoethyl)benzoate (**6c**),<sup>6</sup> 9-diazo-9H-fluorene,<sup>7</sup> (Z)-1,2-diphenyldiazene (**Z-16**),<sup>8</sup> (E)-1,2-bis(4-methoxyphenyl)diazene,<sup>9</sup> (E)-1,2-bis(4-fluorophenyl)diazene,<sup>9</sup> (E)-1,2-bis(4-(trifluoromethyl)phenyl)diazene,<sup>10</sup> (E)-1,2-bis(3,5-dimethylphenyl)diazene,<sup>9,11</sup> (E)-1,2-di-*p*-tolylidiazene,<sup>9</sup> dioctyl 4,4'-(diazene-1,2-diyl)(E)-dibenzoate,<sup>12</sup> (E)-1,2-bis(2,6-dimethylphenyl)diazene,<sup>13</sup> (E)-1,2-bis(3-methoxyphenyl)diazene,<sup>9,10</sup> (E)-1-(*p*-tolyl)-2-(4-(trifluoromethyl)phenyl)diazene,<sup>14</sup> (E)-1,2-di-*o*-tolylidiazene,<sup>9</sup> (E)-1,1'-(diazene-1,2-diylbis(3,1-phenylene))bis(ethan-1-one),<sup>9,15</sup> (E)-1,2-bis(4-azidophenyl)diazene<sup>16</sup>.

**Dioctyl 3,3'-(diazene-1,2-diyl)(E)-dibenzoate.** *n*-Octanol (1.1 mL, 6.99 mmol) and pyridine (1.0 mL, 12.36 mmol) were added to a solution of (E)-3,3'-(diazene-1,2-diyl)dibenzoyl chloride (897 mg, 2.92 mmol)<sup>17</sup> in toluene (30 mL) and the resulting mixture was stirred at reflux temperature for 3 h. The mixture was poured onto an ice-water (150 mL) and the aqueous phase was extracted with toluene (3 × 60 mL). The combined organic layers were washed with HCl (2 M, 60 mL) and deionized water (2 × 40 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The crude material was purified by flash chromatography (silica, hexane/EtOAc, 20:1) to give the title compound as a bright orange solid (1.28 g, 89%). M.p.: 45–

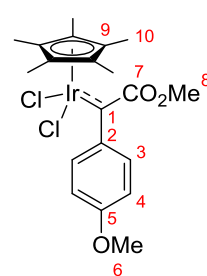


46 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.60 (t,  $J$  = 1.7 Hz, 2 H), 8.18 (dt,  $J$  = 7.8 Hz,  $J$  = 1.4 Hz, 2 H), 8.12 (ddd,  $J$  = 7.9 Hz,  $J$  = 2.0 Hz,  $J$  = 1.2 Hz, 2 H), 7.61 (t,  $J$  = 7.9 Hz, 2 H), 4.38 (t,  $J$  = 6.7 Hz, 4 H), 1.86–1.76 (m, 4 H), 1.53–1.22 (m, 20 H), 0.88 (t,  $J$  = 6.9 Hz, 6 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.2, 152.6, 132.2, 132.0, 129.4, 126.7, 124.7, 65.7, 31.9, 29.4, 29.3, 28.9, 26.2, 22.8, 14.2; IR (film):  $\tilde{\nu}$  = 2949, 2920, 2853, 1718, 1467, 1441, 1285, 1269, 1210, 1153, 1103, 969, 924, 754, 688; MS (EI, %):  $m/z$  = 495 (33), 494  $[\text{M}]^+$  (100), 365 (23), 261 (4), 253 (5), 123 (7), 105 (22), 91 (18), 69 (12); HRMS (ESI+):  $m/z$ : calculated for  $\text{C}_{30}\text{H}_{42}\text{N}_2\text{O}_4\text{Na}$   $[\text{M}+\text{Na}]^+$ : 517.30368, found: 517.30345.

**(E)-1,2-Bis(4-(prop-1-yn-1-yl)phenyl)diazene.** A mixture of 4-(prop-1-yn-1-yl)aniline (401 mg, 3.06 mmol),<sup>18</sup> CuBr (32.6 mg, 0.23 mmol) and pyridine (0.06 mL, 0.74 mmol) in toluene (12 mL) was stirred under air at 60 °C. After 7 h the solvent was evaporated and the crude material was purified by flash chromatography (silica, hexane/EtOAc, 30:1→20:1) to give the title compound as an orange solid (355 mg, 90%). M.p.: 194–195 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.89–7.78 (m, 4 H), 7.56–7.47 (m, 4 H), 2.09 (s, 6 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 151.5, 132.4, 127.1, 123.0, 89.0, 79.8, 4.7; IR (film):  $\tilde{\nu}$  = 2913, 2251, 2212, 1594, 1494, 1404, 1153, 1100, 846, 558; MS (GC-EI, %):  $m/z$  = 258  $[\text{M}]^+$  (21), 143 (20), 130 (2), 115 (100), 103 (1), 89 (20), 77 (2), 65 (13), 63 (11); HRMS (ESI+):  $m/z$ : calculated for  $\text{C}_{18}\text{H}_{15}\text{N}_2$   $[\text{M}+\text{H}]^+$ : 259.12297, found: 259.12296.

## Structural and Mechanistic Investigations

### Representative Procedure for the Preparation of Iridium Carbene Complexes. Dichloro[2-methoxy-

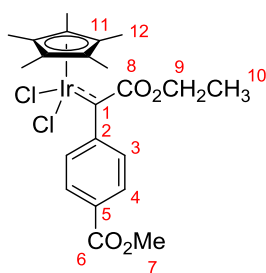


**1-(4-methoxyphenyl)-2-oxoethylidene]( $\eta^5$ -pentamethylcyclopentadienyl)iridium (13).** A solution of the diazo compound **6a** (10.4 mg, 0.050 mmol) in fluorobenzene (0.5 mL) was added dropwise to a solution of  $[\text{Cp}^*\text{IrCl}_2]_2$  (20 mg, 0.025 mmol) in  $\text{CH}_2\text{Cl}_2$  (1 mL) at 0 °C. Crystals suitable for X-ray diffraction were grown by layering this solution with cold toluene (1 mL) and hexane (5 mL) at –20 °C.

For the preparation of NMR samples, a solution of the diazo compound in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) was added dropwise to an ice-cold solution of the iridium complex in  $\text{CD}_2\text{Cl}_2$  (1.0 mL). The solution was stirred under cooling in an ice bath for 5 min before it was transferred into an NMR tube.  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 8.16 (s br, 2 H, H3, H3'), 7.11–6.96 (m, 2 H, H4, H4'), 3.98 (s, 3 H, H6), 3.93 (s, 3 H, H8), 1.52 (s, 15 H, H10);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 275.9 (C1), 182.8 (C7), 169.1 (C5), 150.0 (C2), 116.4 (C4, C4'), 97.7 (C9), 57.1 (C6), 51.0 (C8), 8.3 (C10); one signal (C3, C3') was not detected (probably very broad); HRMS (ESI+):  $m/z$ : calcd. for  $\text{C}_{20}\text{H}_{25}\text{O}_3\text{ClIr}$   $[\text{M}-\text{Cl}]^+$ : 541.11196; found: 541.11229.

The following compounds were prepared analogously:

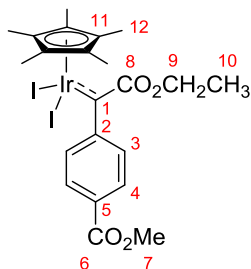
**Dichloro[2-ethoxy-1-(4-(methoxycarbonyl)phenyl)-2-oxoethylidene]( $\eta^5$ -pentamethylcyclopentadienyl)iridium (**14a**).**



Prepared according to the representative procedure from diazo compound **6c** (12.5 mg, 0.050 mmol) and  $[\text{Cp}^*\text{IrCl}_2]_2$  (19 mg, 0.017 mmol).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  = 8.16–8.06 (m, 4 H), 4.45 (s br, 2 H), 3.91 (s, 3 H), 1.46 (s, 15 H), 1.34 (t,  $J$  = 7.2 Hz, 3 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  = 275.4 (C1), 185.0 (C8), 166.4 (C6), 160.4 (C2), 133.9 (C5), 131.1 (C4, C4'), 130.8 (s br, C3, C3'), 101.6 (C11), 61.1 (C9), 53.0 (C7), 14.4 (C10), 8.9 (C12); HRMS (ESI+):  $m/z$ : calcd. for  $\text{C}_{22}\text{H}_{27}\text{O}_4\text{ClIr}$   $[\text{M}-\text{Cl}]^+$ :

583.12253; found: 583.12226.

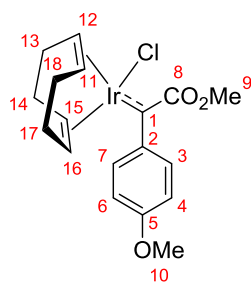
**Diiodo[2-ethoxy-1-(4-(methoxycarbonyl)phenyl)-2-oxoethylidene]( $\eta^5$ -pentamethylcyclopentadienyl)iridium (**14b**).**



Prepared according to the representative procedure from diazo compound **6c** (8.5 mg, 0.034 mmol) and  $[\text{Cp}^*\text{IrI}_2]_2$  (20 mg, 0.017 mmol).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  = 8.14–8.10 (m, 2 H, H3, H3'), 8.00–7.96 (m, 2 H, H4, H4'), 4.42 (q,  $J$  = 7.2 Hz, 2 H, H9), 3.90 (s, 3 H, H7), 1.70 (s, 15 H, H12), 1.32 (t,  $J$  = 7.2 Hz, 3 H, H10);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  = 272.6 (C1), 188.6 (C8), 166.6 (C6), 162.8 (C2), 133.9 (C5), 130.9 (C4, C4'), 129.4 (C3, C3'), 102.4 (C11), 61.0 (C9), 53.0 (C7), 14.1 (C10),

10.4 (C12); HRMS (ESI+):  $m/z$ : calcd. for  $\text{C}_{22}\text{H}_{27}\text{O}_4\text{Ir}$   $[\text{M}-\text{I}]^+$ : 675.05815; found: 675.05852.

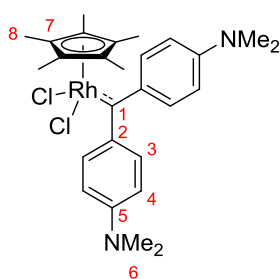
**Chloro[(1,2,5,6- $\eta$ )-1,5-cyclooctadiene][2-methoxy-1-(4-methoxyphenyl)-2-oxoethylidene]iridium (**15**).**



Prepared according to the representative procedure from diazo compound **6a** (12.3 mg, 0.060 mmol) and  $[\text{IrCl}(\text{cod})]_2$  (20 mg, 0.030 mmol).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 8.23 (s br, 2 H, ), 7.02–6.94 (m, 2 H), 5.41 (s br, 2 H), 3.99 (s, 3 H), 3.90 (s br, 3 H), 3.78 (s br, 1 H), 3.45 (s br, 1 H), 2.63–2.06 (m br, 8 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 288.1 (C1), 182.0 (C8), 165.8 (C5), 148.9 (C2), 138.9 (s br, C3, C7), 117.1 (C4, C6), 102.6 (s br, C15), 102.4 (s br, C16), 64.5 (s br C11, C12), 56.7 (C10), 51.8 (C9), 34.5 (s br, C13), 33.5 (s br,

C18), 29.2 (s br, C14), 28.5 (s br, C17); HRMS (ESI+):  $m/z$ : calcd. for  $\text{C}_{18}\text{H}_{22}\text{O}_3\text{Ir}$   $[\text{M}-\text{Cl}]^+$ : 479.11963; found: 479.11954.

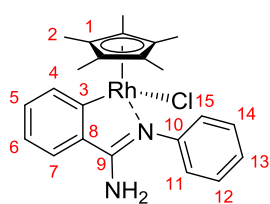
**Dichloro[bis(4-(dimethylamino)phenyl)methylidene]( $\eta^5$ -pentamethylcyclopentadienyl)rhodium (**12**).**



Prepared according to the representative procedure from diazo compound **5b** (18.9 mg, 0.067 mmol) and  $[\text{Cp}^*\text{RhCl}_2]_2$  (21.5 mg, 0.035 mmol).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  = 7.60–7.55 (m, 4 H, H3), 6.64–6.60 (m, 4 H, H4), 3.13 (s, 12 H, H6), 1.35 (s, 15 H, H8);  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  = 291.8 (d,  $J$  = 34.3 Hz, C1), 154.5 (C5), 144.2 (C2), 137.8 (C3), 109.1 (C4), 98.2 (d,  $J$  = 6.3 Hz, C7), 40.3 (C6), 9.2 (C8);  $^{15}\text{N}$

NMR (50 MHz,  $\text{CD}_2\text{Cl}_2$ , 243 K):  $\delta$  = –308.6 (the  $^{15}\text{N}$  resonance were observed by  $^1\text{H}/^{15}\text{N}$ -HMBC spectroscopy); HRMS (ESI+):  $m/z$ : calcd. for  $\text{C}_{27}\text{H}_{35}\text{Cl}_2\text{N}_2\text{Rh}$   $[\text{M}-\text{Cl}]^+$ : 525.15383; found: 525.15469.

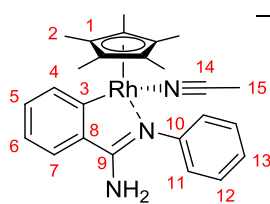
**Chloro[2-(*N'*-phenylcarbamimidoyl- $\kappa$ *N'*)phenyl]( $\eta^5$ -pentamethylcyclopentadienyl)rhodium (**4**).** *N*-



Phenylbenzamidine (33.2 mg, 0.169 mmol), [Cp\* $\text{RhCl}_2$ ]<sub>2</sub> (49.5 mg, 0.080 mmol) and NaOAc (41.0 mg, 0.500 mmol) in toluene (3 mL) were stirred overnight at reflux temperature. The volatiles were removed in vacuo and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (5 × 3 mL). The solution was concentrated until a precipitate formed, which was collected by filtration

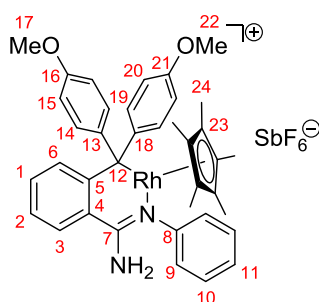
and dried in vacuo to give **4** as an orange powder (47 mg, 63%). Crystals suitable for X-ray diffraction were grown by slow diffusion of *n*-pentane into a solution of **4** in CH<sub>2</sub>Cl<sub>2</sub>. M.p.: >250 °C; <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.72 (dd,  $J$  = 7.6 Hz,  $J$  = 0.9 Hz, 1 H, H4), 7.51 (s br, 2 H, H11, H15), 7.42 (t,  $J$  = 7.8 Hz, 2 H, H12, H14), 7.24 (dd,  $J$  = 7.7 Hz,  $J$  = 1.2 Hz, 1 H, H7), 7.23–7.17 (m, 1 H, H13), 7.13 (td,  $J$  = 7.4 Hz,  $J$  = 1.0 Hz, 1 H, H5), 6.80 (t,  $J$  = 7.5 Hz, 1 H, H6), 5.26 (s br, 2 H, NH<sub>2</sub>), 1.32 (s, 15 H, H2); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 179.3 (d,  $J$  = 32.2 Hz, C3), 164.5 (d,  $J$  = 2.9 Hz, C9), 147.8 (C10), 141.3 (C8), 136.9 (C4), 130.6 (C5), 129.7 (s br, C12, C14), 125.8 (C13), 125.0 (s br, C11, C15), 124.4 (C7), 122.5 (C6), 95.5 (d,  $J$  = 6.5 Hz, C1), 8.8 (C2); IR (solid):  $\tilde{\nu}$  = 3420, 3299, 3240, 3214, 3191, 3173, 1631, 1588, 1488, 1418, 738, 702; HRMS (EI):  $m/z$ : calcd. For C<sub>23</sub>H<sub>26</sub>N<sub>2</sub>ClRh [M]<sup>+</sup>: 468.08325; found: 468.08340.

**(Acetonitrile) [2-(*N'*-phenylcarbamimidoyl- $\kappa$ *N'*)phenyl]( $\eta^5$ -pentamethylcyclopentadienyl)rhodium**



**hexafluoroantimonat (**2**).** [Cp\* $\text{Rh}(\text{MeCN})_3$ ](SbF<sub>6</sub>)<sub>2</sub> (51.1 mg, 0.061 mmol), NaOAc (50.3 mg, 0.613 mmol) and *N*-phenylbenzamidine (12.7 mg, 0.065 mmol) in MeCN (5 mL) were stirred at reflux temperature for 1 h. The volatiles were removed in vacuo. The residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 × 2 mL) and filtered

over Celite. The volatiles were removed in vacuo and the residue was washed with Et<sub>2</sub>O (2 × 0.5 mL). Upon drying in vacuo the residue solidified and complex **2** was obtained as a red orange powder (35 mg, 80%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.82 (dd,  $J$  = 7.6 Hz,  $J$  = 0.6 Hz, 1 H, H4), 7.60–7.53 (m, 2 H, H12, H12'), 7.40 (td,  $J$  = 7.4 Hz,  $J$  = 1.3 Hz, 1 H, H5), 7.37–7.31 (m, 2 H, H7, H13), 7.27–7.17 (m, 3 H, H6, H11), 5.67 (s br, 2 H, NH<sub>2</sub>), 2.27 (s, 3 H, H15), 1.40 (s, 15 H, H2); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 174.5 (d,  $J$  = 30.2 Hz, C3), 165.7 (d,  $J$  = 2.9 Hz, C9), 146.4 (C10), 141.1 (C8), 136.7 (C4), 130.7 (C12, C12'), 127.1 (C13), 124.9 (C7), 124.4 (C11, C11'), 124.2 (C6), 122.6 (s br, C14), 97.9 (d,  $J$  = 6.5 Hz, C1), 8.8 (C2), 3.9 (C15); IR (solid):  $\tilde{\nu}$  = 3488, 3396, 3058, 2975, 2912, 1629, 1586, 1546, 1488, 1450, 1414, 1024, 731, 653; HRMS (ESI):  $m/z$ : calcd. For C<sub>25</sub>H<sub>29</sub>N<sub>3</sub>Rh [M–SbF<sub>6</sub>]<sup>+</sup>: 474.14110; found: 474.14154.

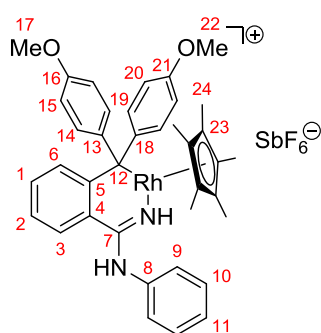


**[Bis(4-methoxyphenyl)(2-(*N'*-phenylcarbamimidoyl- $\kappa$ *N'*)phenyl)methyl]( $\eta^5$ -pentamethylcyclopentadienyl)rhodium(I) hexafluoroantimonat (**3**).** Prepared according to the representative procedure from diazo compound **5a** (7.7 mg, 0.030 mmol) and complex **2** (20.5 mg, 0.029 mmol) at –20 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273 K):  $\delta$  = 7.89–7.81 (m, 1 H, H3), 7.49–7.38 (m, 3 H, H1, H2, H6), 7.34–7.27 (m,



2 H, H10, H10'), 7.26–7.16 (m, 1 H, H20), 7.19–7.12 (m, 3 H, H11, H14, H14'), 7.06 (dd,  $J = 8.0$  Hz,  $J = 2.8$  Hz, 1 H, H20'), 6.82 (d,  $J = 8.9$  Hz, 2 H, H15, H15'), 6.70 (dd,  $J = 8.0$  Hz,  $J = 2.5$  Hz, 1 H, H19'), 6.65 (dd,  $J = 9.2$  Hz,  $J = 2.4$  Hz, 1 H, H19), 6.02 (s br, 2 H, H9, H9'), 5.72 (s br, 1 H, NH<sub>2</sub>), 5.23 (s br, 1 H, NH<sub>2</sub>), 4.00 (s, 3 H, H22), 3.82 (s, 3 H, H17), 0.98 (s, 15 H, H24); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273 K):  $\delta = 163.1$  (C21), 159.8 (C7), 158.9 (C16), 148.2 (C8), 143.0 (C4), 138.6 (C13), 133.3 (C6), 132.5 (C11), 131.7 (C1), 131.2 (C19), 130.0 (C10, C10'), 128.9 (C3), 127.4 (C2), 126.7 (C14, C14'), 126.0 (C20), 124.3 (C9, C9'), 113.1 (C15, C15'), 109.9 (C20'), 106.7 (C18), 105.6 (C19'), 99.5 (d,  $J = 7.2$  Hz, C23), 96.7 (d,  $J = 6.3$  Hz, C5), 71.4 (d,  $J = 14.3$  Hz, C12), 56.4 (C22), 55.6 (C17), 8.6 (C24). HRMS (ESI+):  $m/z$ : calcd. for C<sub>38</sub>H<sub>40</sub>N<sub>2</sub>O<sub>2</sub>Rh [M–SbF<sub>6</sub>]<sup>+</sup>: 659.21393; found: 659.21414.

In solution complex **3** is in equilibrium with the isomeric complex **3'**. The ratio **3:3'** was determined to

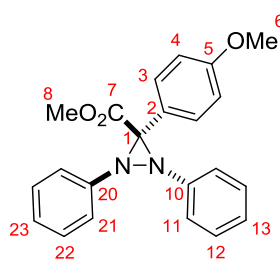


be  $\approx 2.5:1$ . <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273 K):  $\delta = 7.73$  (ddd,  $J = 8.4$  Hz,  $J = 6.7$  Hz,  $J = 1.4$  Hz, 1 H, H2), 7.65 (dd,  $J = 9.0$  Hz,  $J = 1.4$  Hz, 1 H, H6), 7.52–7.46 (m, 2 H, H14, H14'), 7.49–7.38 (m, 1 H, H11), 7.34–7.27 (m, 2 H, H10, H10'), 7.24–7.15 (m, 1 H, H1), 7.19–7.12 (m, 1 H, H3), 7.08 (s br, 1 H, C7–NH–C8), 7.05–6.98 (m, 2 H, H9, H9'), 6.89–6.81 (m, 3 H, H15, H15', H19), 6.57 (dd,  $J = 8.4$  Hz,  $J = 2.5$  Hz, 1 H, H19'), 6.34 (dd,  $J = 8.4$  Hz,  $J = 2.8$  Hz, 1 H, H20), 6.30 (dd,  $J = 8.6$  Hz,  $J = 2.8$  Hz, 1 H, H20'), 6.12 (s br, 1 H, C7–NH), 3.77 (s, 3 H, H17), 3.42 (s, 3 H, H22), 1.39 (s, 15 H, H24);

<sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 273 K):  $\delta = 165.8$  (C8), 158.9 (C7), 158.0 (C16), 157.4 (C21), 138.0 (C13), 136.6 (C18), 134.4 (C6), 133.0 (C19), 132.4 (C14, C14'), 132.3 (C11), 129.5 (C3), 128.7 (C10, C10', C19'), 127.1 (C2), 126.6 (C9, C9'), 126.1 (C1), 115.9 (C4), 114.2 (C20), 113.5 (C15, C15'), 112.4 (C20'), 97.6 (d,  $J = 6.9$  Hz, C23), 91.8 (d,  $J = 4.2$  Hz, C5), 84.1 (d,  $J = 13.2$  Hz, C12), 55.4 (C17), 55.2 (C22), 8.8 (C24).

**Stoichiometric NMR Experiments.** A cold (0 °C) solution of diazo compound **6a** (9.1 mg, 0.044 mmol) in degassed CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added dropwise to a cold (0 °C) solution of [Cp\*<sup>+</sup>RhI<sub>2</sub>]<sub>2</sub> (21.6 mg, 0.022 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (1 mL). The mixture was stirred for 10 min whilst cooling in an ice bath before it was cooled to –78 °C and solid (*Z*)-**16** (8.5 mg, 0.047 mmol) was added in one portion. After 5 min this mixture was transferred to a precooled (–78 °C) NMR tube.

**Methyl 3-(4-methoxyphenyl)-1,2-diphenyldiaziridine-3-carboxylate (41).** A cold (0 °C) solution of



the diazo compound **6a** (9.4 mg, 0.046 mmol) in degassed CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added dropwise to an ice-cold solution of [Cp\*<sup>+</sup>RhI<sub>2</sub>]<sub>2</sub> (22.4 mg, 0.023 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (1 mL) and the resulting mixture was stirred for 15 min whilst cooling in an ice bath. The mixture was cooled to –78 °C before solid (*Z*)-**16** (8.8 mg, 0.048 mmol) was added in one portion and the resulting mixture was stored at –40 °C overnight. The mixture was layered

with precooled (–40 °C) and carefully degassed *n*-pentane (1.5 mL) and stored at the same temperature, which resulted in precipitation of a red solid material. The mother liquor was transferred into another precooled (–40 °C) Schlenk tube, layered with precooled (–40 °C) *n*-pentane

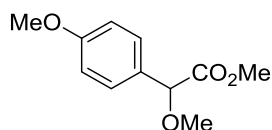


(2 mL), and slowly cooled to  $-78\text{ }^{\circ}\text{C}$  to give the title compound in the form of small colorless crystals suitable for X-ray diffraction. The material analyzed as follows:  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_2\text{Cl}_2$ , 233 K):  $\delta = 7.35\text{--}7.29$  (m, 2 H, H22, H22'), 7.29–7.25 (m, 2 H, H3, H3'), 7.25–7.21 (m, 2 H, H21, H21'), 7.19–7.13 (m, 1 H, H23), 7.13–7.07 (m, 2 H, H12, H12'), 6.98–6.92 (m, 3 H, H11, H11', H13), 6.76–6.70 (m, 2 H, H4, H4'), 3.69 (s, 3 H, H6), 3.45 (s, 3 H, H8);  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CD}_2\text{Cl}_2$ , 233 K):  $\delta = 166.4$  (C7), 159.9 (C5), 148.3 (C20), 147.1 (C10), 129.9 (C3, C3'), 128.6 (C22, C22'), 128.2 (C12, C12'), 125.0 (C23), 124.1 (C13), 122.5 (C2), 120.7 (C11, C11'), 120.0 (C21, C21'), 113.1 (C4, C4'), 73.4 (C1), 55.2 (C6), 52.9 (C8);  $^{15}\text{N}$  NMR (50 Hz,  $\text{CD}_2\text{Cl}_2$ , 233 K):  $\delta = -252.2$  (N1),  $-263.2$  (the  $^{15}\text{N}$  resonances were observed by  $^1\text{H}/^{15}\text{N}$ -HMBC spectroscopy). HRMS (ESI+):  $m/z$ : calculated for  $\text{C}_{22}\text{H}_{21}\text{N}_2\text{O}_3$   $[\text{M}+\text{H}]^+$ : 361.15467, found: 361.15439.

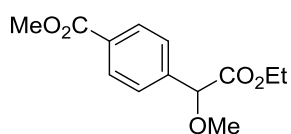
## Substrate and Catalyst Screening

### Representative Procedure for the Iridium Catalyzed Insertion of Diazo Compounds into O–H Bonds.

**Methyl 2-methoxy-2-(4-methoxyphenyl)acetate (9a, X = OMe).** The diazo derivative **6a** (20.0 mg, 0.097 mmol) was added in portions to a solution of  $[\text{Cp}^*\text{IrCl}_2]_2$  (1.0 mg, 1.3  $\mu\text{mol}$ ) and methanol (39  $\mu\text{L}$ , 0.970 mmol) in pentane (3 mL). After consumption of the starting material, as indicated by TLC, the reaction mixture was concentrated in vacuo. The residue was purified by flash chromatography (silica, hexane/EtOAc, 10:1→5:1) to give the title compound as a light yellow oil (15 mg, 74%). The spectral data matched the previously reported values.<sup>19</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.38\text{--}7.32$  (m, 2 H), 6.92–6.86 (m, 2 H), 4.72 (s, 1 H), 3.80 (s, 3 H), 3.71 (s, 3 H), 3.37 (s, 3 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 171.5, 160.1, 128.7, 128.3, 114.2, 82.2, 57.2, 55.4, 52.4$ .

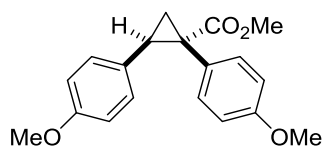


**Methyl 4-(2-ethoxy-1-methoxy-2-oxoethyl)benzoate (9b, X = COOEt).** Prepared analogously in the form of a light orange oil (48 mg, 90%). The spectral data matched the previously reported values.<sup>20</sup>  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.06\text{--}8.01$  (m, 2 H), 7.56–7.51 (m, 2 H), 4.81 (s, 1 H), 4.24–4.19 (m, 2 H), 3.91 (s, 3 H), 3.43 (s, 3 H), 1.21 (t,  $J = 7.1$  Hz, 3 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 170.2, 166.9, 141.4, 130.6, 130.0, 127.2, 82.4, 61.7, 57.7, 52.3, 14.2$ .



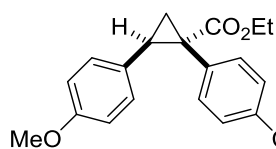
### Procedures for the Iridium Catalyzed Cyclopropanation of 4-Methoxystyrene with Diazo Compounds.

**Methyl (E)-1,2-bis(4-methoxyphenyl)cyclopropane-1-carboxylate (7a).** The diazo compound **6a** (20.0 mg, 0.097 mmol) was added in one portion to a solution of  $[\text{Cp}^*\text{IrCl}_2]_2$  (1.0 mg, 1.3  $\mu\text{mol}$ ) and 4-methoxystyrene (120 mg, 0.894 mmol) in  $\text{CH}_2\text{Cl}_2$  (3 mL) and the resulting mixture was stirred at  $40\text{ }^{\circ}\text{C}$ . After consumption of the starting material, as indicated by TLC, the mixture was concentrated in vacuo. The residue was purified by flash chromatography (silica, hexane/EtOAc, 5:1) to give the title compound as a colorless liquid (19 mg, 63%). The spectral data



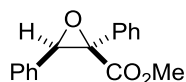
matched the previously reported values.<sup>21</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 6.96–6.91 (m, 2 H), 6.71–6.68 (m, 2 H), 6.68–6.66 (m, 2 H), 6.64–6.59 (m, 2 H), 3.73 (s, 3 H), 3.71 (s, 3 H), 3.65 (s, 3 H), 3.02 (dd, *J* = 9.4 Hz, *J* = 7.3 Hz, 1 H), 2.10 (dd, *J* = 9.4 Hz, *J* = 4.8 Hz, 1 H), 1.75 (dd, *J* = 7.3 Hz, *J* = 4.8 Hz, 1 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 174.9, 158.5, 158.2, 133.1, 129.2, 128.6, 127.1, 113.3 (2 C), 55.2 (2 C), 52.7, 36.4, 32.9, 21.0.

**Methyl 4-((*E*)-1-(ethoxycarbonyl)-2-(4-methoxyphenyl)cyclopropyl)benzoate (7b).** A solution of the



diazo compound **6c** (49.3 mg, 0.199 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added *via* syringe pump over the course of 1 h to a solution of [Cp\*IrI<sub>2</sub>]<sub>2</sub> (2.3 mg, 2.0 μmol) and 4-methoxystyrene (0.26 mL, 1.96 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). After consumption of the starting material (TLC), the mixture was concentrated in vacuo. The residue was purified by flash chromatography (silica, hexane/EtOAc, 5:1→5:2) to give the title compound as a light orange oil (41 mg, 58%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.83–7.78 (m, 2 H), 7.13–7.08 (m, 2 H), 6.71–6.67 (m, 2 H), 6.62–6.57 (m, 2 H), 4.20–4.06 (m, 2 H), 3.86 (s, 3 H), 3.69 (s, 3 H), 3.09 (dd, *J* = 9.4 Hz, *J* = 7.3 Hz, 1 H), 2.13 (dd, *J* = 9.4 Hz, *J* = 5.0 Hz, 1 H), 1.84 (dd, *J* = 7.3 Hz, *J* = 5.0 Hz, 1 H), 1.16 (t, *J* = 7.1 Hz, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 173.3, 167.2, 158.4, 140.7, 132.1, 129.1, 129.1, 128.8, 127.9, 113.5, 61.5, 55.3, 52.2, 37.2, 32.9, 20.1, 14.3; IR (liquid):  $\tilde{\nu}$  = 2982, 2953, 2907, 2837, 1711, 1611, 1514, 1436, 1275, 1173, 159, 1103, 1020, 831, 706; MS (EI, %): *m/z* = 534 [M]<sup>+</sup> (100), 325 (26), 308 (61), 281 (66), 279 (29), 265 (11), 249 (35), 221 (31), 207 (10), 189 (13), 178 (19), 165 (21), 145 (11), 137 (12), 121 (13), 115 (13); HRMS (ESI<sup>+</sup>): *m/z*: calculated for C<sub>21</sub>H<sub>22</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup>: 377.13594, found: 377.13562.

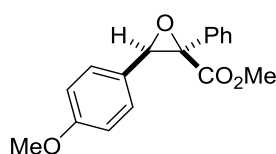
**Representative Procedure for the Rhodium Catalyzed Epoxidation Reactions. Methyl (Z)-2,3-diphenyloxirane-2-carboxylate (Table 2, entry 1).** A solution of the diazo



compound **6b** (67.3 mg, 0.382 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added *via* syringe pump over the course of 1 h to a solution of benzaldehyde (26.0 mg, 0.250 mmol) and [Cp\*RhI<sub>2</sub>]<sub>2</sub> (2.8 mg, 1.2 μmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). After consumption of the starting material, as indicated by TLC, the mixture was concentrated in vacuo. The residue was purified by flash chromatography (silica, hexane/EtOAc, 20:1→10:1) to give the title compound as a colorless oil (39 mg, 63%). The spectral data matched the previously reported values.<sup>22</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.67–7.63 (m, 2 H), 7.45–7.33 (m, 8 H), 4.16 (s, 1 H), 3.55 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 167.2, 134.8, 133.9, 129.0, 128.8, 128.7, 128.5, 126.3, 126.1, 67.2, 66.0, 52.4.

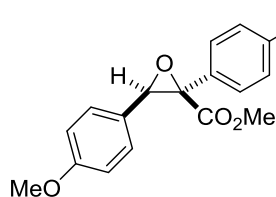
The following compounds were prepared analogously:

**Methyl (Z)-3-(4-methoxyphenyl)-2-phenyloxirane-2-carboxylate (Table 2, entry 4).** Colorless oil



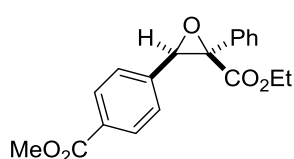
(62 mg, 96%). The spectral data matched the previously reported values.<sup>23</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.66–7.61 (m, 2 H), 7.43–7.35 (m, 3 H), 7.34–7.29 (m, 2 H), 6.92–6.87 (m, 2 H), 4.10 (s, 1 H), 3.82 (s, 3 H), 3.58 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 167.4, 160.0, 134.9, 128.9, 128.7, 127.4, 126.3, 125.9, 114.0, 67.2, 65.9, 55.4, 52.4.

**Methyl (Z)-2,3-bis(4-methoxyphenyl)oxirane-2-carboxylate (Table 2, entry 5).** Colorless liquid



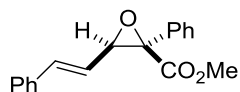
(65 mg, 83%). The spectral data matched the previously reported values.<sup>24</sup> Crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a solution in EtOAc at 5 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.57–7.52 (m, 2 H), 7.34–7.28 (m, 2 H), 6.95–6.91 (m, 2 H), 6.91–6.86 (m, 2 H), 4.09 (s, 1 H), 3.82 (s, 3 H), 3.81 (s, 3 H), 3.57 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 191.0, 167.6, 160.1, 159.9, 127.7, 127.4, 126.9, 125.9, 114.1, 113.9, 67.0, 65.8, 55.5, 55.4, 52.3.

**Ethyl (Z)-3-(4-(methoxycarbonyl)phenyl)-2-phenyloxirane-2-carboxylate (Table 2, entry 6).** Colorless



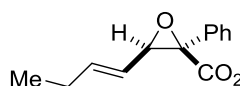
oil (69 mg, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.08–8.02 (m, 2 H), 7.67–7.61 (m, 2 H), 7.51–7.46 (m, 2 H), 7.45–7.39 (m, 3 H), 4.19 (s, 1 H), 3.93 (s, 3 H), 3.54 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 166.9, 166.8, 138.9, 134.4, 130.6, 129.8, 129.2, 128.8, 126.3, 126.2, 67.3, 65.4, 52.5, 52.4; IR (liquid):  $\tilde{\nu}$  = 3063, 3032, 3001, 2953, 1717, 1613, 1435, 1274, 1216, 1193, 1167, 1101, 757, 738, 696; MS (EI, %): *m/z* = 312 [M]<sup>+</sup> (1), 284 (2), 281 (3), 253 (1), 225 (<1), 221 (<1), 194 (1), 193 (1), 179 (100), 165 (4), 148 (4), 133 (2), 120 (1), 105 (17), 89 (3), 77 (7), 63 (1); HRMS (ESI<sup>+</sup>): *m/z*: calculated for C<sub>18</sub>H<sub>16</sub>O<sub>5</sub>Na [M+Na]<sup>+</sup>: 335.08899, found: 335.08869.

**Methyl (Z)-2-phenyl-3-((E)-styryl)oxirane-2-carboxylate (Table 2, entry 7).** Colorless oil (58 mg,



88%). The spectral data matched the previously reported values.<sup>25</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.62–7.58 (m, 2 H), 7.43–7.27 (m, 8 H), 6.90 (d, *J* = 16.0 Hz, 1 H), 6.09 (dd, *J* = 16.0 Hz, *J* = 7.9 Hz, 1 H), 3.82 (s, 3 H), 3.73 (dd, *J* = 7.9 Hz, *J* = 0.6 Hz, 1 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 168.3, 137.5, 135.9, 134.9, 128.9, 128.7, 128.6, 126.9, 126.7, 122.0, 65.9, 65.6, 52.9.

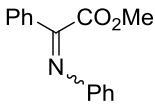
**Methyl (Z)-3-((E)-but-1-en-1-yl)-2-phenyloxirane-2-carboxylate (Table 2, entry 8).** Colorless liquid

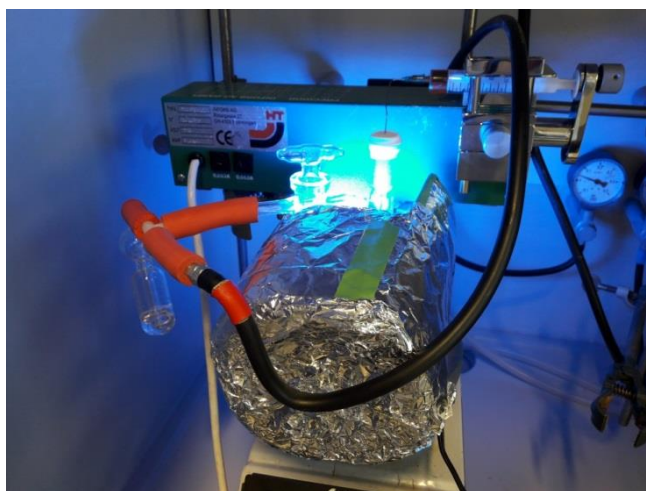


(64 mg, 99%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.60–7.53 (m, 2 H), 7.41–7.30 (m, 3 H), 6.11 (dt, *J* = 15.5 Hz, *J* = 6.4 Hz, 1 H), 5.33 (ddt, *J* = 15.5 Hz, *J* = 8.1 Hz, *J* = 1.6 Hz, 1 H), 3.81 (s, 3 H), 3.53 (d, *J* = 8.1 Hz, 1 H), 2.19–2.08 (m, 2 H), 1.02 (t, *J* = 7.5 Hz, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 168.5, 142.1, 135.2, 128.7, 128.5, 126.7, 122.0, 65.8, 65.2, 52.7, 25.7, 13.2; IR (liquid):  $\tilde{\nu}$  = 2964, 1736, 1435, 1302, 1279, 1200, 1112, 966, 753, 697, 640; MS (GC-EI, %): *m/z* = 232 [M]<sup>+</sup> (<1), 216 (1), 187 (4), 173 (8), 157 (6), 155 (7), 145 (25), 129 (15), 117 (12), 115 (16), 105 (51), 99 (100), 91 (15), 77 (42), 67 (24); HRMS (ESI<sup>+</sup>): *m/z*: calculated for C<sub>14</sub>H<sub>16</sub>O<sub>3</sub>Na [M+Na]<sup>+</sup>: 255.09916, found: 255.09906.

## Metathesis of Azobenzene Derivatives

### Representative Procedure for the Rhodium Catalyzed Metathesis between Diazo Compounds and Azoarenes Performed at Ambient Temperature. Methyl (Z)-2-phenyl-2-(phenylimino)acetate (17).

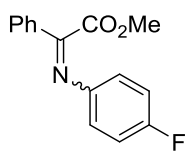
 A solution of the diazo compound **6b** (113.2 mg, 0.643 mmol) in toluene (2 mL) was added *via* syringe pump over the course of 2 h to a solution of azobenzene **16** (44.8 mg, 0.250 mmol) and [Cp\**Rh*I<sub>2</sub>]<sub>2</sub> (2.3 mg, 2.3 μmol) in toluene (3 mL) during constant irradiation of the mixture with the light emitted by blue LEDs (Figure S5). After consumption of the starting material, as indicated by TLC, the mixture was concentrated in vacuo. The residue was purified by flash chromatography (silica, hexane/EtOAc, 20:1 + 1% Et<sub>3</sub>N) to give the title compound as an orange oil (107 mg, mixture of two geometric isomers (95:5), 91%). The spectral data of the major isomer matched the previously reported values.<sup>26</sup> Crystals suitable for X-ray diffraction were grown by storing a saturated solution in *n*-pentane in a fridge. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.90–7.85 (m, 2 H), 7.56–7.44 (m, 3 H), 7.37–7.31 (m, 2 H), 7.17–7.11 (m, 1 H), 6.99–6.94 (m, 2 H), 3.64 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 165.6, 160.1, 150.2, 134.0, 132.0, 129.0, 128.9, 128.1, 125.1, 119.6, 52.0.



**Figure S5:** Experimental set-up for the rhodium catalyzed metathesis between diazo compounds and azoarenes performed at ambient temperature: Schlenk flask with septum in the center, syringe pump (in green) with syringe in the back, self-made LED array (see Figure S4) wrapped in aluminum foil, and argon supply (black tubing).

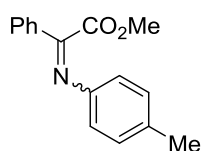
The following compounds were prepared analogously:

### Methyl (Z)-2-((4-fluorophenyl)imino)-2-phenylacetate (21).

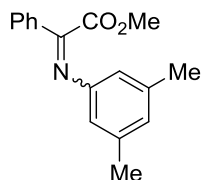
 Yellow oil (119 mg, mixture of two geometric isomers (94:6), 91%). The spectral data of the major isomer are given. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.88–7.84 (m, 2 H), 7.56–7.50 (m, 1 H), 7.50–7.44 (m, 2 H), 7.07–7.00 (m, 2 H), 6.97–6.90 (m, 2 H), 3.67 (s); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 165.6, 160.6, 160.5 (d, <sup>1</sup>J<sub>CF</sub> = 243.8 Hz), 146.3 (d, <sup>4</sup>J<sub>CF</sub> = 2.8 Hz), 133.8, 132.1, 128.9, 128.1, 121.3 (d, <sup>3</sup>J<sub>CF</sub> = 8.1 Hz), 115.8 (d, <sup>2</sup>J<sub>CF</sub> = 22.5 Hz), 52.1; <sup>19</sup>F{<sup>1</sup>H}-NMR (282 MHz,

CDCl<sub>3</sub>):  $\delta$  = -118.4; IR (liquid):  $\tilde{\nu}$  = 3066, 3031, 2953, 1732, 1499, 1229, 1214, 1192, 1170, 1009, 844, 769, 689; MS (EI, %):  $m/z$  = 257 [M]<sup>+</sup> (12), 240 (2), 199 (13), 198 (100), 181 (1), 151 (1.03), 104 (1), 103 (1), 95 (14), 91 (5), 77 (6), 75 (7); HRMS (ESI<sup>+</sup>):  $m/z$ : calculated for C<sub>15</sub>H<sub>12</sub>NO<sub>2</sub>F [M+H]<sup>+</sup>: 258.09248, found: 258.09232.

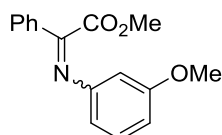
**Methyl (Z)-2-phenyl-2-(p-tolylimino)acetate (18).** Orange oil (124 mg, mixture of two geometric isomers (94:6), 97%). The spectral data of the major isomer are given. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.90–7.84 (m, 2 H), 7.55–7.43 (m, 3 H), 7.17–7.11 (m, 2 H), 6.92–6.87 (m, 2 H), 3.68 (s, 3 H), 2.34 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.9, 159.7, 147.6, 134.8, 134.1, 131.8, 129.6, 128.8, 128.0, 119.7, 52.0, 21.1; IR (liquid):  $\tilde{\nu}$  = 3027, 2952, 2923, 1732, 1624, 1504, 1449, 1433, 1301, 1225, 1194, 1166, 1009, 908, 838, 729; MS (GC-EI, %):  $m/z$  = 253 [M]<sup>+</sup> (8), 195 (16), 194 (100), 165 (1), 152 (<1), 116 (1), 103 (3), 97 (2), 91 (36), 77 (5), 65 (30), 63 (5), 51 (5), 39 (8); HRMS (ESI<sup>+</sup>):  $m/z$ : calculated for C<sub>16</sub>H<sub>16</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 254.11755, found: 254.11727.



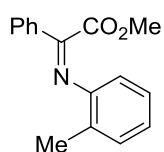
**Methyl (Z)-2-((3,5-dimethylphenyl)imino)-2-phenylacetate (26).** Orange-yellow oil (130 mg, mixture of two geometric isomers (94:6), 95%). The spectral data of the major isomer are given. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.89–7.83 (m, 2 H), 7.55–7.43 (m, 3 H), 6.81–6.77 (m, 1 H), 6.63–6.58 (m, 2 H), 3.68 (s, 3 H), 2.31 (s, 6 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.8, 159.5, 150.1, 138.7, 134.1, 131.8, 128.8, 128.1, 126.9, 117.4, 51.9, 21.4; IR (liquid):  $\tilde{\nu}$  = 2950, 2917, 1732, 1603, 1588, 1449, 1432, 1317, 1280, 1208, 1142, 1025, 848, 687; MS (GC-EI, %):  $m/z$  = 267 [M]<sup>+</sup> (10), 209 (16), 208 (100), 193 (1), 166 (<1), 105 (15), 103 (11), 97 (5), 79 (13), 77 (16), 65 (2), 51 (2); HRMS (ESI<sup>+</sup>):  $m/z$ : calculated for C<sub>17</sub>H<sub>18</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 268.13320, found: 268.13299.



**Methyl (Z)-2-((3-methoxyphenyl)imino)-2-phenylacetate (24).** Yellow oil (135 mg, mixture of two geometric isomers (98:2), 99%). The spectral data of the major isomer are given. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.90–7.84 (m, 2 H), 7.55–7.50 (m, 1 H), 7.50–7.44 (m, 2 H), 7.26–7.20 (m, 1 H), 6.71 (ddd, <sup>3</sup>J = 8.4 Hz, <sup>4</sup>J = 2.4 Hz, <sup>4</sup>J = 1.0 Hz, 1 H), 7.25–7.20 (m, 2 H), 3.80 (s, 3 H), 3.67 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.6, 160.2, 160.1, 151.5, 133.9, 132.0, 129.9, 128.9, 128.1, 111.7, 111.3, 105.4, 55.4, 52.1; IR (liquid):  $\tilde{\nu}$  = 3064, 3003, 2952, 2835, 1731, 1592, 1579, 1480, 1432, 1210, 1139, 1009, 776, 688; MS (GC-EI, %):  $m/z$  = 269 [M]<sup>+</sup> (11), 211 (15), 210 (100), 195 (2), 167 (2), 107 (10), 105 (5), 92 (20), 77 (24), 64 (11), 51 (2); HRMS (ESI<sup>+/-</sup>):  $m/z$ : calculated for C<sub>16</sub>H<sub>16</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 270.11247, found: 270.11198.

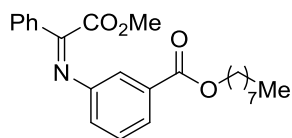


**Methyl (Z)-2-phenyl-2-(o-tolylimino)acetate (23).** Yellow oil (109 mg, one isomer, 85%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.94–7.89 (m, 2 H), 7.54–7.45 (m, 3 H), 7.22–7.18 (m, 1 H), 7.16–7.10 (m, 1 H), 7.05 (td,  $J$  = 7.4 Hz,  $J$  = 1.2 Hz, 1 H), 6.74–6.70 (m, 1 H), 3.61 (s, 3 H), 2.22 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 165.5, 159.5, 149.1, 133.9, 131.9, 130.3, 129.3, 128.9, 128.1, 126.3, 125.0, 117.5, 51.9, 18.1; IR (liquid):  $\tilde{\nu}$  = 3064, 3025, 2951, 1733, 1629, 1596, 1578, 1484, 1449, 1433, 1304, 1229, 1203, 1171, 1111, 1009, 754,



689; MS (GC-EI, %):  $m/z$  = 253 [ $M$ ]<sup>+</sup> (13), 195 (15), 194 (100), 167 (6), 165 (3), 152 (1), 116 (4), 103 (3), 91 (40), 89 (9), 77 (4), 65 (32), 51 (4); HRMS (ESI<sup>+</sup>):  $m/z$ : calculated for C<sub>16</sub>H<sub>16</sub>NO<sub>2</sub> [ $M+H$ ]<sup>+</sup>: 254.11755, found: 254.11744.

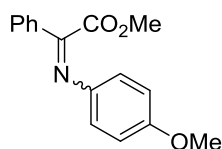
**Octyl (Z)-3-((2-methoxy-2-oxo-1-phenylethylidene)amino)benzoate (25).** Yellow oil (169 mg, one isomer, 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.91–7.86 (m, 2 H), 7.84 (ddd,



$J$  = 7.8 Hz,  $J$  = 1.5 Hz,  $J$  = 1.2 Hz, 1 H), 7.68–7.64 (m, 1 H), 7.57–7.51 (m, 1 H), 7.51–7.45 (m, 2 H), 7.41 (td,  $J$  = 7.8 Hz,  $J$  = 0.3 Hz, 1 H), 7.15 (ddd,  $J$  = 7.8 Hz,  $J$  = 2.2 Hz,  $J$  = 1.1 Hz, 1 H), 4.31 (t,  $J$  = 6.7 Hz, 2 H), 3.66 (s, 3 H),

1.81–1.71 (m, 2 H), 1.49–1.39 (m, 2 H), 1.39–1.20 (m, 8 H), 0.88 (t,  $J$  = 6.8 Hz, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 166.4, 165.2, 160.9, 150.2, 133.7, 132.2, 131.5, 129.1, 128.9, 128.2, 126.3, 124.1, 120.8, 65.4, 52.1, 31.9, 29.4, 29.3, 28.8, 26.2, 22.8, 14.2; IR (liquid):  $\tilde{\nu}$  = 2953, 2926, 2855, 1736, 1717, 1625, 1580, 1450, 1433, 1266, 1171, 1103, 1011, 757, 688; MS (EI, %):  $m/z$  = 396 (2), 395 [ $M$ ]<sup>+</sup> (7), 337 (24), 336 (100), 266 (3), 224 (15), 179 (4), 65 (1); HRMS (ESI<sup>+</sup>):  $m/z$ : calculated for C<sub>24</sub>H<sub>30</sub>NO<sub>4</sub> [ $M+H$ ]<sup>+</sup>: 396.21693, found: 396.21668.

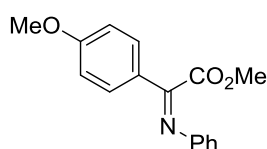
**Methyl (Z)-2-((4-methoxyphenyl)imino)-2-phenylacetate (19).** Yellow solid (103 mg, mixture of two



geometric isomers (93:7), 77%). The spectral data of the major isomer matched the previously reported values.<sup>27</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.89–7.83 (m, 2 H), 7.54–7.42 (m, 3 H), 7.00–6.94 (m, 2 H), 6.92–6.85 (m, 2 H), 3.81 (s, 3 H), 3.70 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 166.3, 159.3, 157.5, 143.3,

134.3, 131.7, 128.8, 128.0, 121.3, 114.3, 55.6, 52.1.

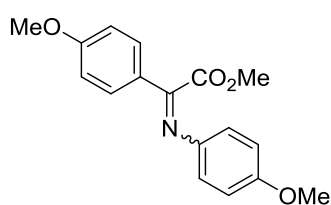
**Methyl (Z)-2-(4-methoxyphenyl)-2-(phenylimino)acetate (31).** Yellow oil (130 mg, one isomer, 97%).



<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 7.85–7.80 (m, 2 H), 7.35–7.29 (m, 2 H), 7.15–7.09 (m, 1 H), 7.00–6.93 (m, 2 H), 3.88 (s, 3 H), 3.63 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 165.9, 163.1, 159.6, 150.8, 130.1, 129.3, 126.9, 125.1,

120.0, 114.5, 55.9, 52.1; IR (liquid):  $\tilde{\nu}$  = 2953, 2839, 1735, 1602, 1591, 1513, 1259, 1164, 1016; MS (GC-EI, %):  $m/z$  = 269 [ $M$ ]<sup>+</sup> (9), 211 (15), 210 (100), 195 (5), 167 (9), 133 (6), 103 (3), 90 (5), 77 (55), 63 (4), 51 (21); HRMS (ESI<sup>+</sup>):  $m/z$ : calculated for C<sub>16</sub>H<sub>16</sub>NO<sub>3</sub> [ $M+H$ ]<sup>+</sup>: 270.11239, found: 270.11247.

**Methyl (Z)-2-(4-methoxyphenyl)-2-((4-methoxyphenyl)imino)acetate (32).** Yellow solid (103 mg,



mixture of two geometric isomers ( $\approx$ 85:15), 69%). The spectral data of the major isomer is given. M.p.: 91–92 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.84–7.77 (m, 2 H), 7.00–6.91 (m, 4 H), 6.90–6.83 (m, 2 H), 3.87 (s, 3 H), 3.80 (s, 3 H), 3.67 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 166.4, 162.5, 158.7, 157.2, 143.6, 129.8, 127.0, 121.3, 114.3, 114.2, 55.6, 55.5,

52.0; IR (film):  $\tilde{\nu}$  = 3012, 2973, 2953, 2937, 2914, 2839, 1729, 1604, 1594, 1572, 1510, 1498, 1452, 1309, 1244, 1160, 1022, 842, 510; MS (EI, %):  $m/z$  = 299 [ $M$ ]<sup>+</sup> (19), 241 (15), 240 (100), 225 (6), 197 (5), 154 (<1), 120 (2), 92 (4), 77 (3); HRMS (GC-EI):  $m/z$ : calculated for C<sub>17</sub>H<sub>17</sub>NO<sub>4</sub> [ $M$ ]<sup>+</sup>: 299.11521, found: 299.11523.

**Methyl (Z)-4-(2-ethoxy-2-oxo-1-(phenylimino)ethyl)benzoate (34).** Yellow oil (140 mg, mixture of two geometric isomers (96:4), 90%). The spectral data of the major isomer is given. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.16–8.10 (m, 2 H), 7.99–7.94 (m, 2 H), 7.36–7.30 (m, 2 H), 7.19–7.13 (m, 1 H), 6.99–6.94 (m, 2 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 3.95 (s, 3 H), 0.99 (t, *J* = 7.1 Hz, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 166.5, 164.6, 159.4, 150.0, 137.8, 132.9, 130.0, 129.0, 128.1, 125.4, 119.6, 61.8, 52.5, 13.8; IR (liquid):  $\tilde{\nu}$  = 2983, 2953, 1721, 1624, 1435, 1274, 1223, 1187, 1106, 1014, 761, 696; MS (GC-EI, %): *m/z* = 311 [M]<sup>+</sup> (3), 280 (1), 239 (13), 238 (74), 179 (6), 152 (2), 130 (3), 104 (4), 77 (100), 51 (13); HRMS (ESI<sup>+</sup>): *m/z*: calculated for C<sub>18</sub>H<sub>17</sub>NO<sub>4</sub>Na [M+Na]<sup>+</sup>: 334.10498, found: 334.10484.

**Methyl (Z)-4-(2-ethoxy-1-((4-methoxyphenyl)imino)-2-oxoethyl)benzoate (35).** Yellow solid (113 mg, mixture of two geometric isomers (94:6), 66%). The spectral data of the major isomer is given. M.p.: 75–76 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.14–8.09 (m, 2 H), 7.97–7.91 (m, 2 H), 7.01–6.95 (m, 2 H), 6.92–6.86 (m, 2 H), 4.20 (q, *J* = 7.1 Hz, 2 H), 3.95 (s, 3 H), 3.81 (s, 3 H), 1.09 (t, *J* = 7.1 Hz, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 166.6, 165.4, 158.5, 157.8, 143.0, 138.2, 132.6, 130.0, 127.9, 121.4, 114.3, 61.8, 55.6, 52.5, 14.0; IR (film):  $\tilde{\nu}$  = 3007, 2981, 2959, 2838, 1713, 1630, 1499, 1434, 1288, 1240, 1224, 1189, 1105, 1014, 708; MS (EI, %): *m/z* = 341 [M]<sup>+</sup> (14), 269 (16), 268 (100), 253 (2), 225 (2), 209 (3), 166 (<1), 119 (1), 92 (4), 77 (4); HRMS (GC-EI): *m/z*: calculated for C<sub>19</sub>H<sub>19</sub>NO<sub>5</sub> [M]<sup>+</sup>: 341.12577, found: 341.12566.

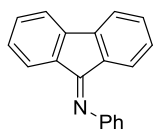
**Methyl (Z)-2-phenyl-2-((4-(prop-1-yn-1-yl)phenyl)imino)acetate (29).** Orange oil (90 mg, mixture of two geometric isomers (93:7), 65%). The spectral data of the major isomer is given. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.90–7.83 (m, 2 H), 7.56–7.50 (m, 1 H), 7.50–7.43 (m, 2 H), 7.40–7.34 (m, 2 H), 6.92–6.85 (m, 2 H), 3.64 (s, 3 H), 2.06 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 165.4, 160.1, 149.4, 133.8, 132.3, 132.1, 128.9, 128.2, 120.8, 119.7, 85.8, 79.7, 52.1, 4.5; IR (liquid):  $\tilde{\nu}$  = 3062, 3035, 2951, 2915, 2850, 1731, 1623, 1498, 1226, 1195, 1165, 1007, 848, 688, 561; MS (GC-EI, %): *m/z* = 277 [M]<sup>+</sup> (23), 219 (16), 218 (100), 203 (1), 140 (<1), 115 (14), 109 (1), 89 (5), 77 (1), 65 (2), 63 (2); HRMS (ESI<sup>+</sup>): *m/z*: calculated for C<sub>18</sub>H<sub>16</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 278.11755, found: 278.11757.

**Methyl (Z)-2-((4-azidophenyl)imino)-2-phenylacetate (30).** Yellow oil (100 mg, mixture of two geometric isomers (93:7), 71%). The spectral data of the major isomer is given. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.89–7.83 (m, 2 H), 7.56–7.50 (m, 1 H), 7.50–7.44 (m, 2 H), 7.04–6.96 (m, 4 H), 3.69 (s, 3 H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ = 165.6, 160.4, 147.2, 136.9, 133.8, 132.1, 128.9, 128.1, 121.4, 119.7, 52.2; IR (liquid):  $\tilde{\nu}$  = 3062, 3035, 2951, 2108, 2077, 1731, 1621, 1497, 1294, 1226, 1195, 1166, 1006, 841, 688, 674, 556; MS (EI, %): *m/z* = 280 [M]<sup>+</sup> (10), 253 (17), 252 (100), 221 (8), 208 (6), 207 (36), 194 (5), 193 (30), 192 (19), 180 (10), 168 (3), 167 (4), 166 (5), 141 (1), 140 (3), 139 (2), 129 (1), 120 (1), 118 (3), 115 (2), 106



(9), 105 (5), 104 (4), 103 (3), 97 (2), 90 (29), 80 (21), 77 (10), 63 (12); HRMS (ESI+):  $m/z$ : calculated for  $C_{15}H_{13}N_4O_2$   $[M+H]^+$ : 281.10330, found: 281.10347.

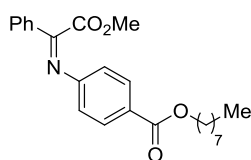
**N-Phenyl-9H-fluoren-9-imine (37).** Yellow oil (66 mg, 67%). The spectral data matched the previously



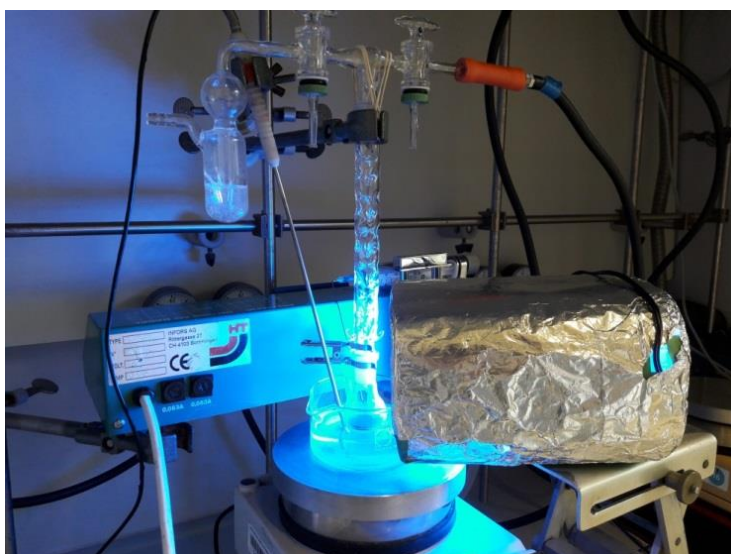
reported values.<sup>28</sup>  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 7.90 (d,  $J$  = 7.5 Hz, 1 H), 7.60–7.52 (m, 2 H), 7.47–7.35 (m, 3 H), 7.35–7.24 (m, 2 H), 7.23–7.14 (m, 1 H), 7.01–6.94 (m, 2 H), 6.88 (td,  $J$  = 7.6 Hz,  $J$  = 1.0 Hz, 1 H), 6.54 (d,  $J$  = 7.7 Hz, 1 H);  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 163.0, 151.9, 143.9, 142.0, 137.6, 132.0, 131.9, 131.3, 129.4, 128.5, 127.8, 127.2, 124.1, 123.4, 120.3, 119.7, 118.4.

### Representative Procedure for the Rhodium Catalyzed Metathesis between Diazo Compounds and Azoarenes at Elevated Temperature.

**Octyl (Z)-4-((2-methoxy-2-oxo-1-phenylethylidene)amino)benzoate (20).** A solution of diazo



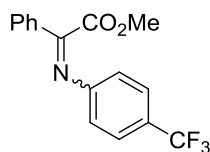
compound **6b** (101.5 mg, 0.576 mmol) in toluene (2 mL) was added *via* syringe pump over the course of 2 h to a solution of dioctyl 4,4'-(diazene-1,2-diyl)(*E*)-dibenzoate (122.9 mg, 0.248 mmol) and  $[Cp^*RhI_2]_2$  (2.2 mg, 2.2  $\mu$ mol) in toluene (13 mL) at 90 °C under constant irradiation with the light emitted by a blue LED (Figure S6). After consumption of the starting material, as indicated by TLC, the mixture was concentrated in vacuo. The residue was purified by flash chromatography (silica, hexane/EtOAc, 20:1 + 1%  $Et_3N$ ) to give the title compound as an orange oil (175 mg, one isomer, 89%). The spectral data of the major isomer matched the previously reported values.  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  = 8.06–8.00 (m, 2 H), 7.90–7.85 (m, 2 H), 7.58–7.51 (m, 1 H), 7.51–7.45 (m, 2 H), 7.01–6.95 (m, 2 H), 4.31 (t,  $J$  = 6.7 Hz), 3.63 (s, 3 H), 1.77 (quint,  $J$  = 6.8 Hz), 1.52–1.23 (m, 12 H), 0.89 (t,  $J$  = 6.9 Hz);  $^{13}C\{^1H\}$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  = 166.5, 164.9, 160.6, 154.3, 133.5, 132.4, 130.7, 129.0, 128.3, 127.1, 119.4, 65.2, 52.2, 31.9, 29.4, 29.3, 28.9, 26.2, 22.8, 14.2; IR (liquid):  $\tilde{\nu}$  = 2953, 2926, 2855, 1736, 1713, 1598, 1269, 1227, 1196, 1163, 1099, 1009, 861, 772, 689; MS (EI, %):  $m/z$  = 395  $[M]^+$  (10), 337 (23), 336 (100), 266 (6), 224 (17), 179 (7), 104 (<1), 103 (<1), 76 (2), 65 (1); HRMS (ESI+):  $m/z$ : calculated for  $C_{24}H_{30}NO_4$   $[M+H]^+$ : 396.216934, found: 396.21649.



**Figure S6.** Experimental set-up for the rhodium catalyzed metathesis between diazo compounds and azoarenes at elevated temperatures: two-neck Schlenk flask in oil bath with septum and vigreux column (centre), syringe pump (in green) with syringe in the back, self-made LED array (see Figure S4) wrapped in aluminum foil, and argon supply (red/black tubing).

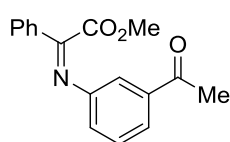
The following compounds were prepared analogously:

**Methyl (Z)-2-phenyl-2-((4-(trifluoromethyl)phenyl)imino)acetate (22).** Orange oil (128 mg, mixture



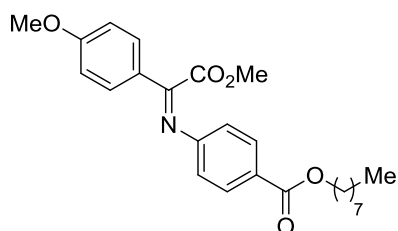
of two geometric isomers (94:6), 84%). The spectral data of the major isomer are given.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.91–7.46 (m, 2 H), 7.63–7.58 (m, 2 H), 7.58–7.53 (m, 1 H), 7.53–7.46 (m, 2 H), 7.06–7.01 (m, 2 H), 3.65 (s, 3 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 164.8, 161.1, 153.2, 133.4, 132.5, 129.0, 128.3, 127.0 (q,  $^2J$  = 32.4 Hz), 126.3 (q,  $^3J$  = 3.7 Hz), 124.4 (q,  $^1J$  = 270.7 Hz), 119.8, 52.2;  $^{19}\text{F}\{^1\text{H}\}$  NMR (282 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -62.1; IR (liquid):  $\tilde{\nu}$  = 3065, 3054, 2955, 1735, 1608, 1319, 1230, 1163, 1063, 1015, 1009, 852, 689; MS (GC-EI, %):  $m/z$  = 307 [ $\text{M}$ ] $^+$  (5), 288 (2), 249 (15), 248 (100), 228 (3), 208 (2), 172 (1), 145 (41), 125 (10), 103 (10), 95 (21), 77 (29), 51 (5); HRMS (ESI+):  $m/z$ : calculated for  $\text{C}_{16}\text{H}_{13}\text{NO}_2\text{F}_3$  [ $\text{M}+\text{H}$ ] $^+$ : 308.08929, found: 308.08901.

**Methyl (Z)-2-((3-acetylphenyl)imino)-2-phenylacetate (28).** Orange oil (116 mg, one isomer, 83%).



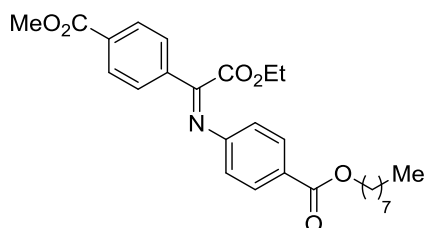
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.90–7.85 (m, 2 H), 7.76 (ddd,  $J$  = 7.8 Hz,  $J$  = 1.7 Hz,  $J$  = 1.1 Hz, 1 H), 7.58–7.52 (m, 2 H), 7.52–7.46 (m, 2 H), 7.44 (t,  $J$  = 7.8 Hz, 1 H), 7.17 (ddd,  $J$  = 7.8 Hz,  $J$  = 2.2 Hz,  $J$  = 1.0 Hz, 1 H), 3.65 (s, 3 H), 2.60 (s, 3 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 197.8, 165.2, 161.1, 150.4, 138.0, 133.6, 132.3, 129.4, 129.0, 128.2, 124.9, 124.3, 119.8, 52.1, 26.9; IR (liquid):  $\tilde{\nu}$  = 3063, 3004, 2952, 1732, 1683, 1624, 1578, 1429, 1262, 1216, 1163, 1010, 687; MS (GC-EI, %):  $m/z$  = 281 [ $\text{M}$ ] $^+$  (7), 223 (16), 222 (100), 179 (2), 119 (5), 104 (7), 103 (5), 91 (40), 77 (21), 76 (32), 65 (12), 50 (10), 43 (29); HRMS (ESI+):  $m/z$ : calculated for  $\text{C}_{17}\text{H}_{16}\text{NO}_3$  [ $\text{M}+\text{H}$ ] $^+$ : 282.11247, found: 282.11272.

**Octyl (Z)-4-((2-methoxy-1-(4-methoxyphenyl)-2-oxoethylidene)amino)benzoate (33).** Orange oil



(138 mg, one isomer, 65%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.05–7.99 (m, 2 H), 7.86–7.79 (m, 2 H), 7.00–6.93 (m, 4 H), 4.30 (t,  $J$  = 6.7 Hz), 3.88 (s, 3 H), 3.61 (s, 3 H), 1.77 (quint,  $J$  = 6.9 Hz), 1.50–1.40 (m, 2 H), 1.40–1.22 (m, 10 H), 0.89 (t,  $J$  = 6.9 Hz);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.6, 165.1, 163.0, 159.8, 154.6, 130.7, 130.2, 126.8, 126.2, 119.6, 114.4, 65.2, 55.6, 52.1, 31.9, 29.4, 29.3, 28.9, 26.2, 22.8, 14.2; IR (liquid):  $\tilde{\nu}$  = 2953, 2927, 2855, 1736, 1712, 1592, 1573, 1513, 1256, 1229, 1158, 1112, 1098, 1017, 839, 772, 704; MS (EI, %):  $m/z$  = 425 [ $\text{M}$ ] $^+$  (3), 425 (9), 368 (4), 367 (22), 366 (100), 296 (4), 254 (14), 209 (5), 118 (1), 76 (<1); HRMS (ESI+):  $m/z$ : calculated for  $\text{C}_{25}\text{H}_{32}\text{NO}_5$  [ $\text{M}+\text{H}$ ] $^+$ : 426.22750, found: 426.22704.

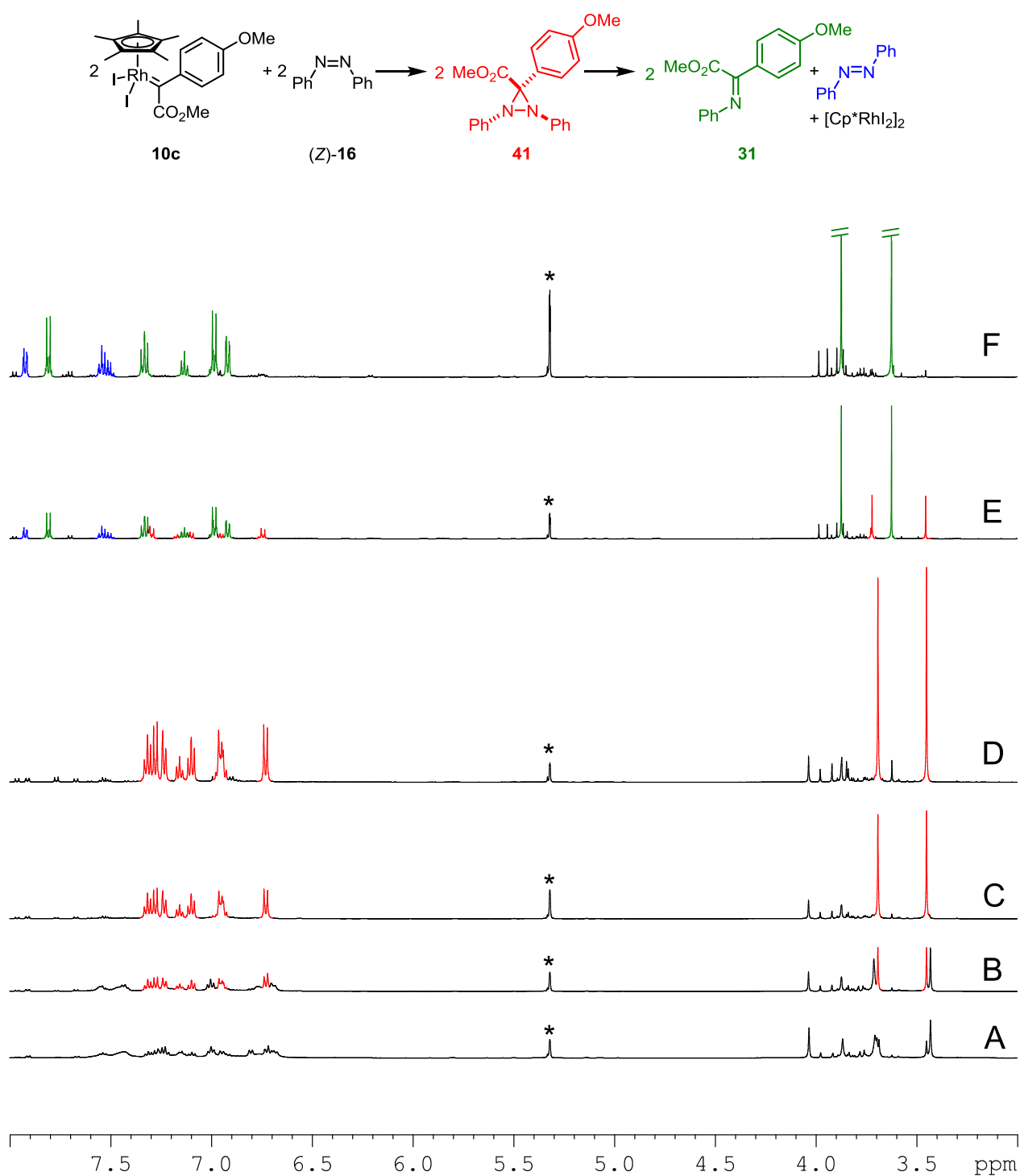
**Methyl (Z)-4-(2-ethoxy-1-((4-((octyloxy)carbonyl)phenyl)imino)-2-oxoethyl)benzoate (36).** Brown



oil (138 mg, one isomer, 38%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.17–8.11 (m, 2 H), 8.06–8.00 (m, 2 H), 7.99–7.94 (m, 2 H), 7.02–6.96 (m, 2 H), 4.14 (q,  $J$  = 7.2 Hz, 2 H), 4.31 (t,  $J$  = 6.7 Hz, 2 H), 3.96 (s, 3 H), 1.83–1.71 (m, 2 H), 1.50–1.40 (m, 2 H), 1.40–1.22 (m, 8 H), 0.88 (t,  $J$  = 6.8 Hz, 3 H);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 166.4 (2 C), 164.0, 159.9, 154.0, 137.3, 133.2, 130.7, 130.1, 128.3, 127.3, 119.3, 65.3, 62.0,

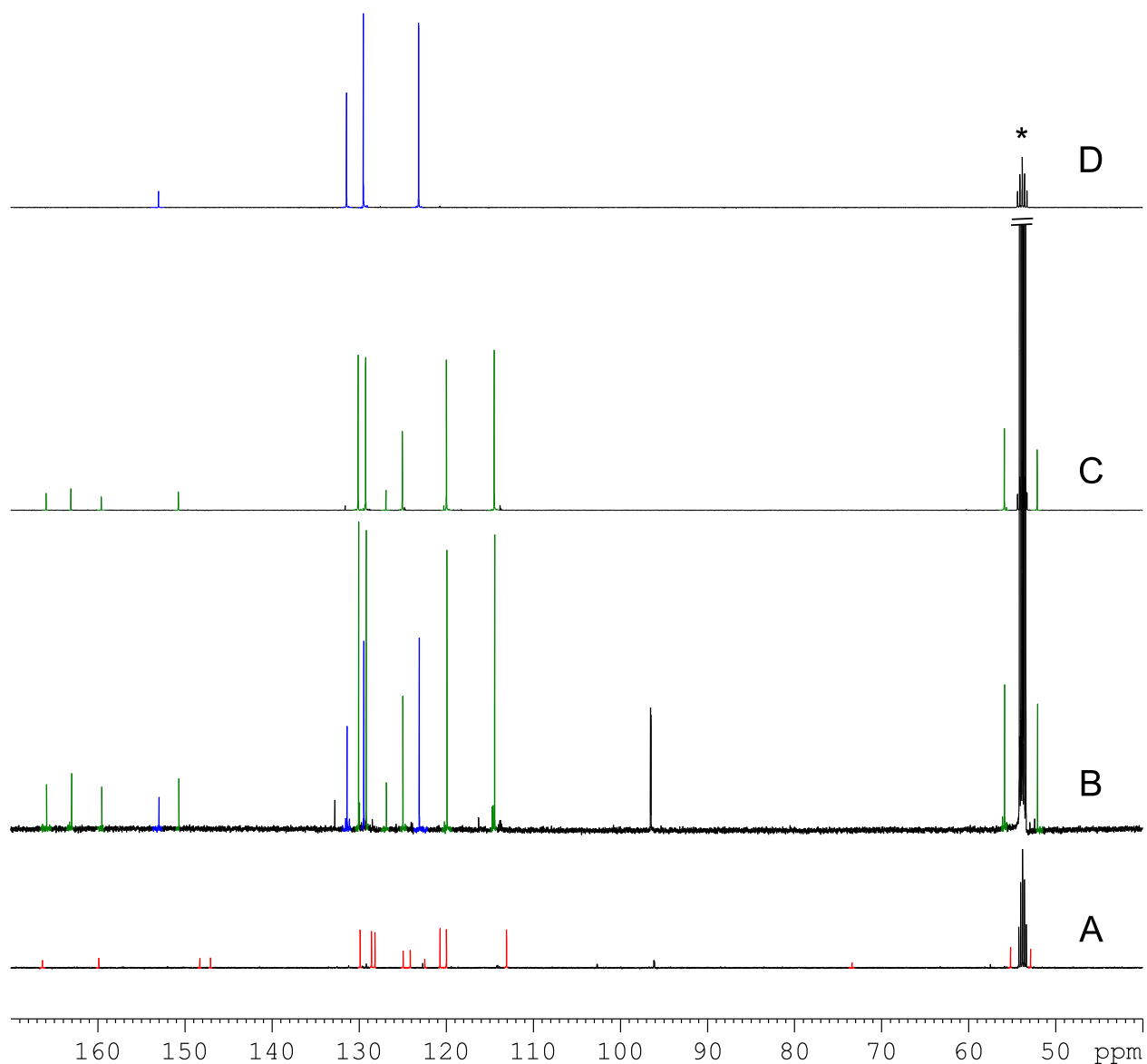
52.6, 31.9, 29.4, 29.3, 28.9, 26.2, 22.8, 14.2, 13.9; IR (liquid):  $\tilde{\nu}$  = 2954, 2927, 2856, 1715, 1600, 1268, 1189, 1164, 1100, 1014, 869, 772, 700; MS (EI, %):  $m/z$  = 467 [M]<sup>+</sup> (5), 436 (2), 395 (24), 394 (100), 338 (4), 282 (12), 237 (4), 179 (<1), 121 (<1), 76 (1); HRMS (ESI+):  $m/z$ : calculated for C<sub>27</sub>H<sub>33</sub>NO<sub>6</sub>Na [M+Na]<sup>+</sup>: 490.22001, found: 490.22002.

**Stoichiometric Low Temperature NMR Experiments for the Characterization of the Diaziridine Intermediate (41).**

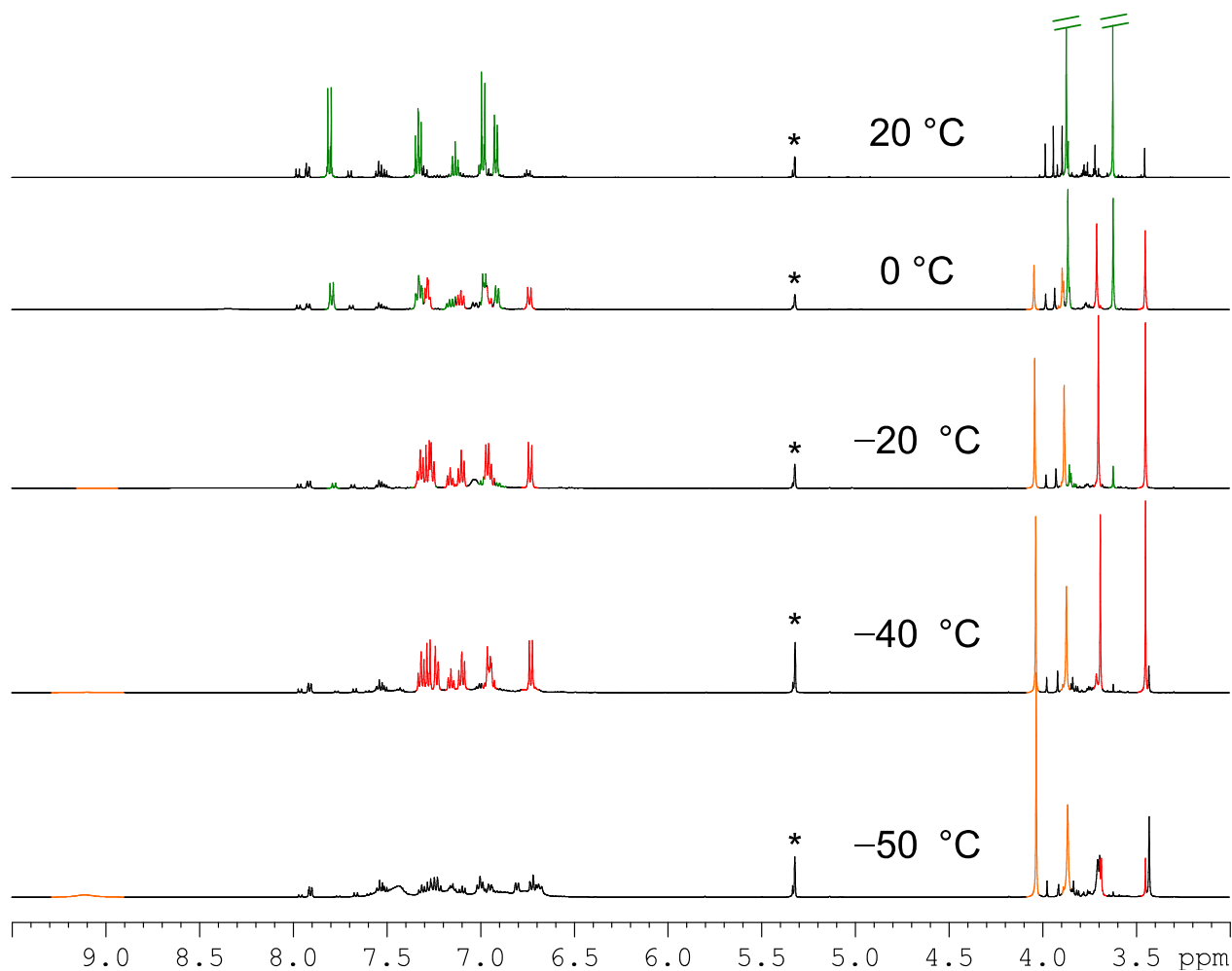
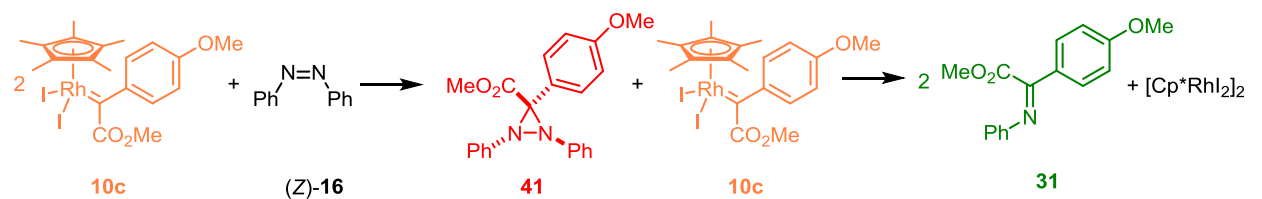


**Figure S7:**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) of the stoichiometric (1:1) reaction of carbene complex **10c** and (Z)-**16** recorded at different temperatures. For an explanation see text below (\* = residual  $\text{CDHCl}_2$  in  $\text{CD}_2\text{Cl}_2$ ). Color coding refers to the structures in the equation at the top of the page.

An ill-defined mixture was observed at the starting point of the experiment ( $-50\text{ }^{\circ}\text{C}$ ,  $t = 0\text{ h}$ , Figure S7-A). Warming this mixture to  $-40\text{ }^{\circ}\text{C}$  over 45 min resulted in the slow formation of the diaziridine intermediate **41** (Figure S7-B). After 3 h at  $-40\text{ }^{\circ}\text{C}$  the formation of **41** was complete (Figure S7-C). **41** was stable at this temperature overnight (Figure S7-D,  $t = 15\text{ h}$ ) allowing full characterization by NMR. Warming the sample to  $25\text{ }^{\circ}\text{C}$  resulted in conversion of **41** to imine **31** and (*E*)-**16** (figure S7-E). After full conversion their ratio was  $\approx 2.9:1$  (figure S7-F) at  $25\text{ }^{\circ}\text{C}$ .



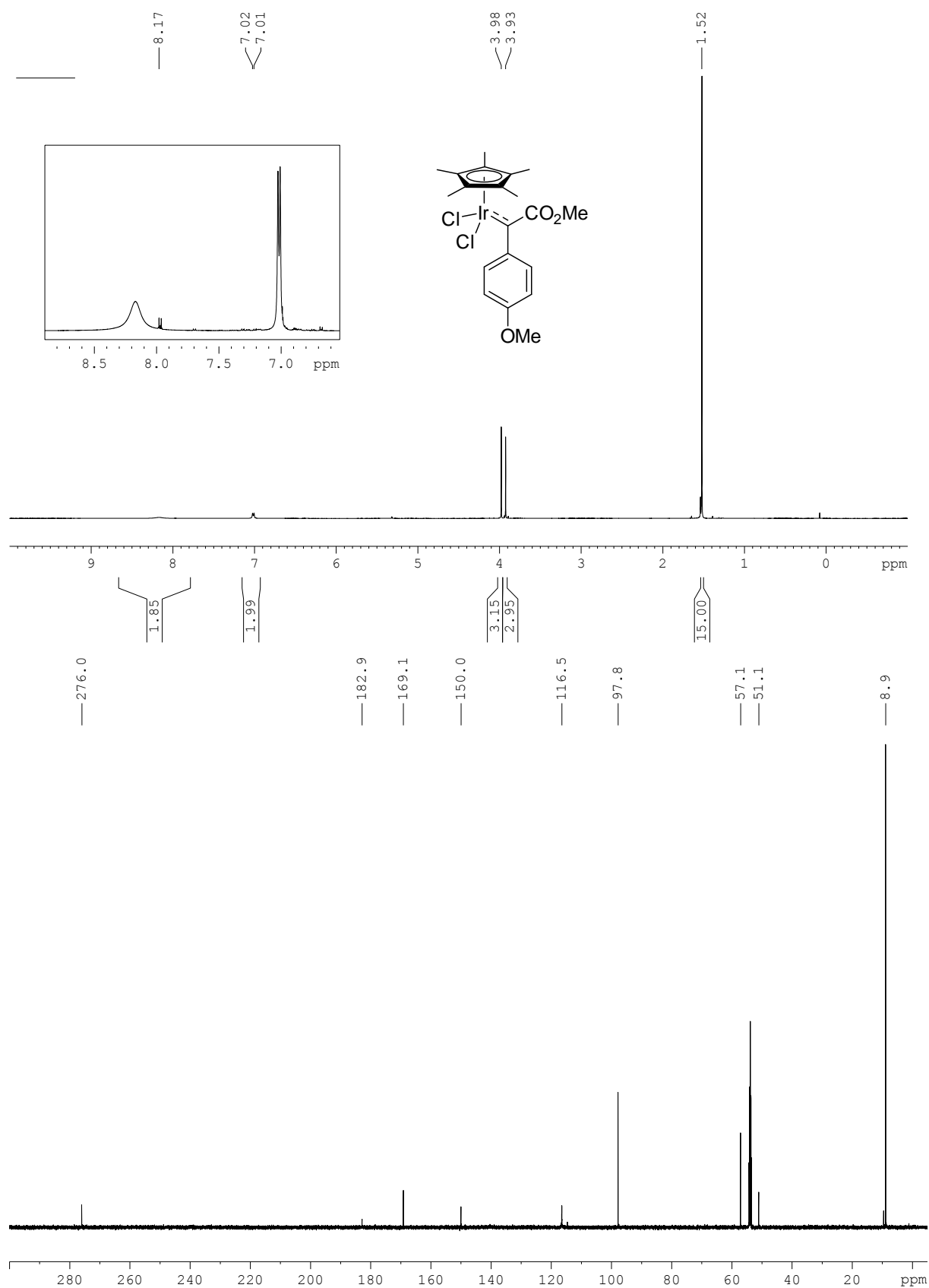
**Figure S8:**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) of the reaction mixture at  $-40\text{ }^{\circ}\text{C}$  ( $t = 3\text{ h}$ ; **A**), the reaction mixture at  $25\text{ }^{\circ}\text{C}$  (**B**; compare Figure S7-F), an isolated sample of imine **31** (**C**) and an isolated sample of (*E*)-**16** (**D**). Color coding refers to the structures in the equation at the top of the previous page.



**Figure S9:**  $^1\text{H}$  NMR spectra (500 MHz,  $\text{CD}_2\text{Cl}_2$ ) of the stoichiometric (2:1) reaction of carbene complex **10c** and (Z)-**16** at different temperatures. For an explanation see text below (\* = residual  $\text{CDHCl}_2$  in  $\text{CD}_2\text{Cl}_2$ ). Color coding refers to the structures in the equation at the top of the page.

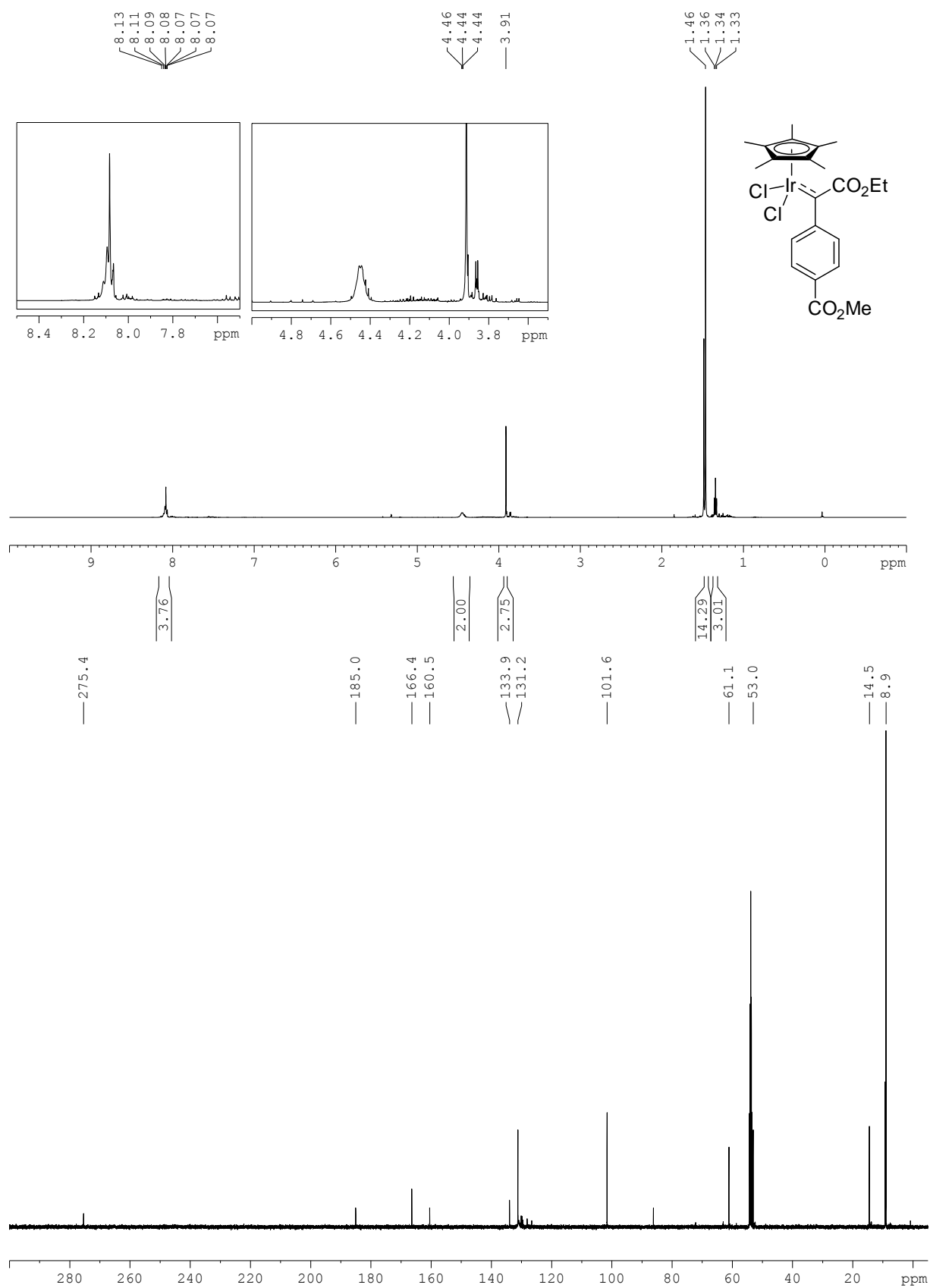
An ill-defined mixture was observed at the starting point of the experiment ( $-50\text{ }^\circ\text{C}$ ). Warming this mixture to  $-40\text{ }^\circ\text{C}$  resulted in the slow formation of 1 equivalent of diaziridine intermediate **41** while 1 equivalent of complex **10c** remained in the solution. Increasing the temperature to ca.  $-25\text{ }^\circ\text{C}$  resulted in the selective conversion of **10c** and **41** to imine **31**. Full conversion was reached at about  $+15\text{ }^\circ\text{C}$ . Only traces of (E)-**16** were observed during the entire experiment.

# Iridium Carbene Complex 13

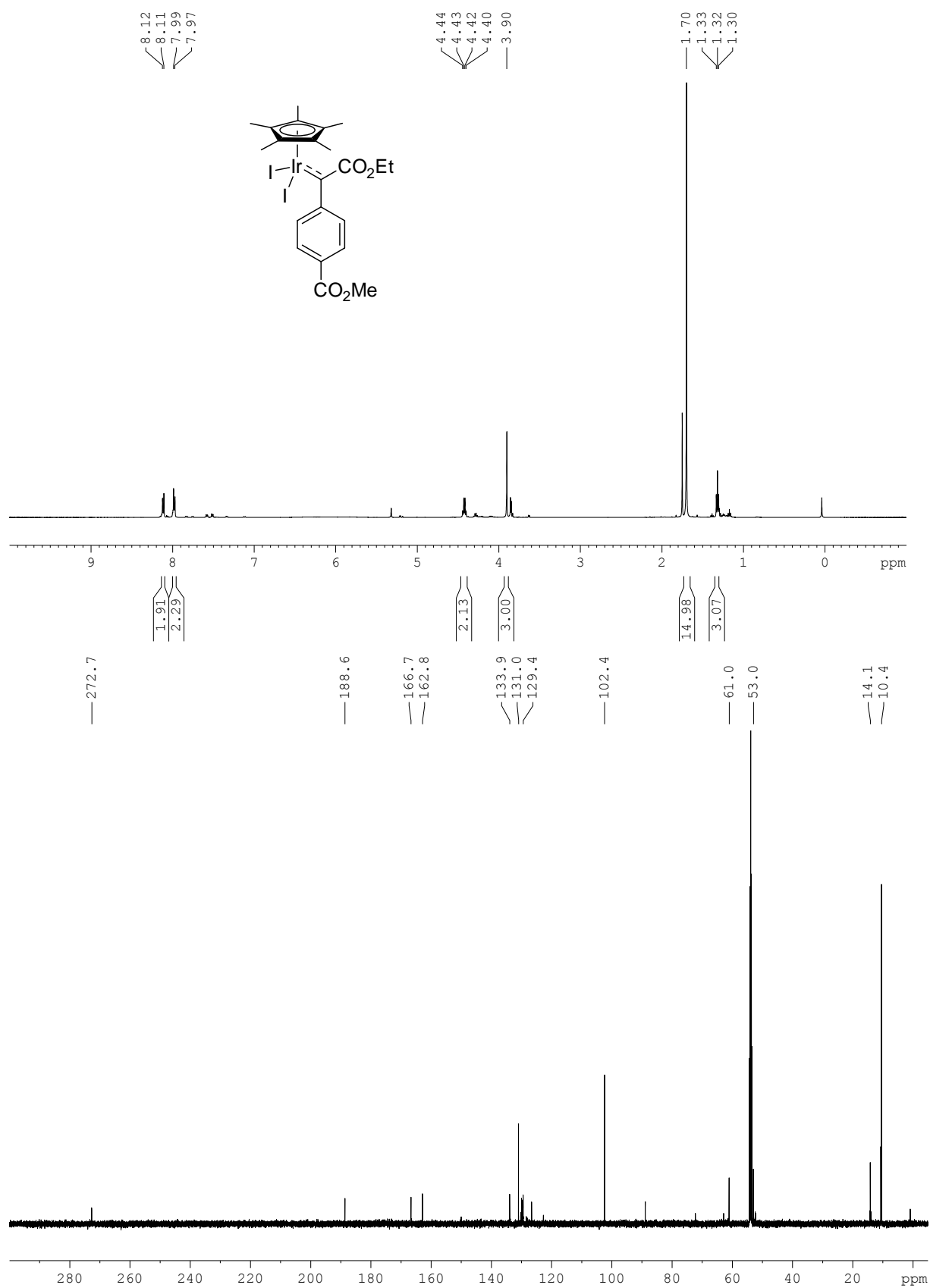




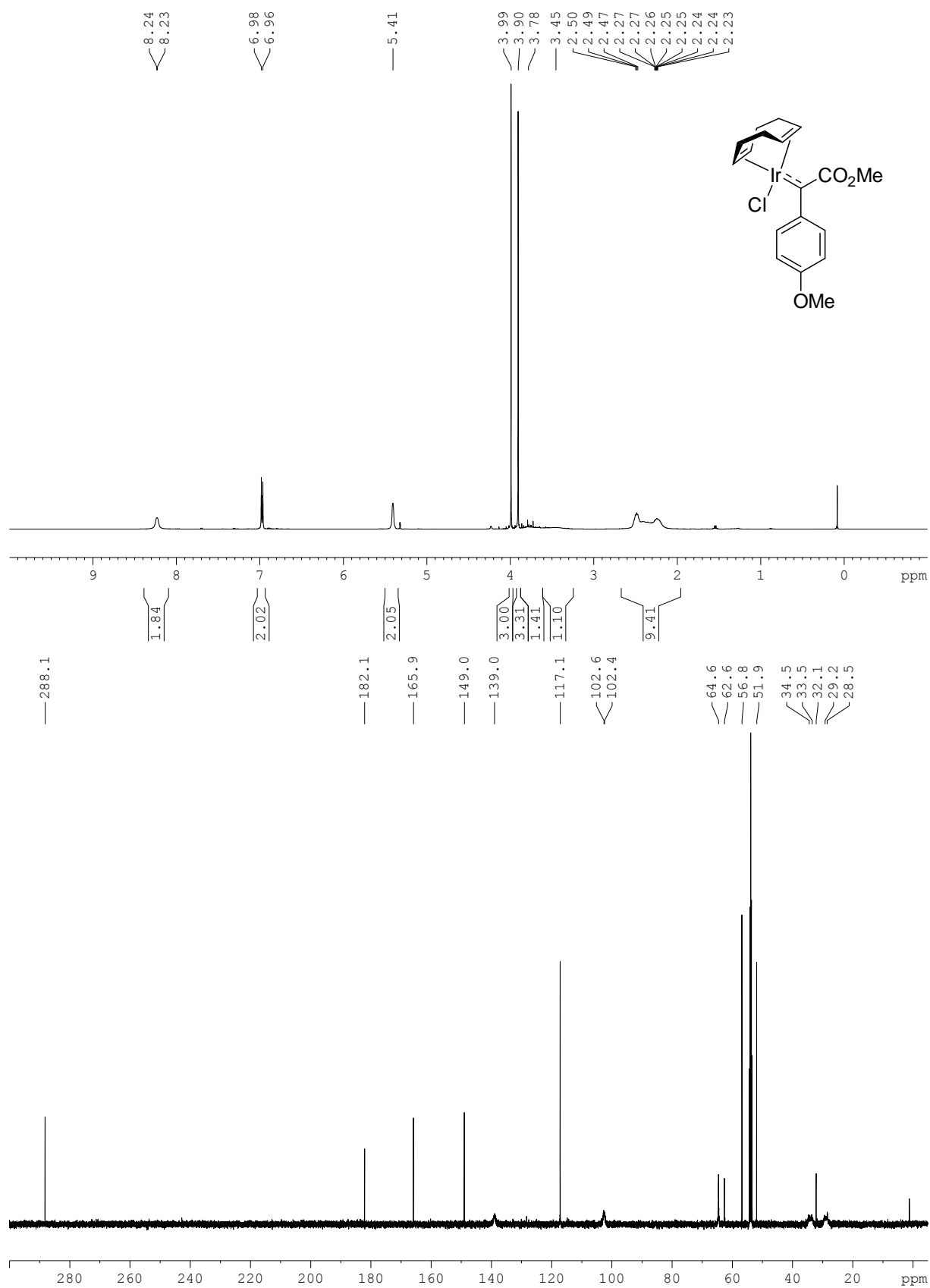
# Iridium Carbene Complex 14a



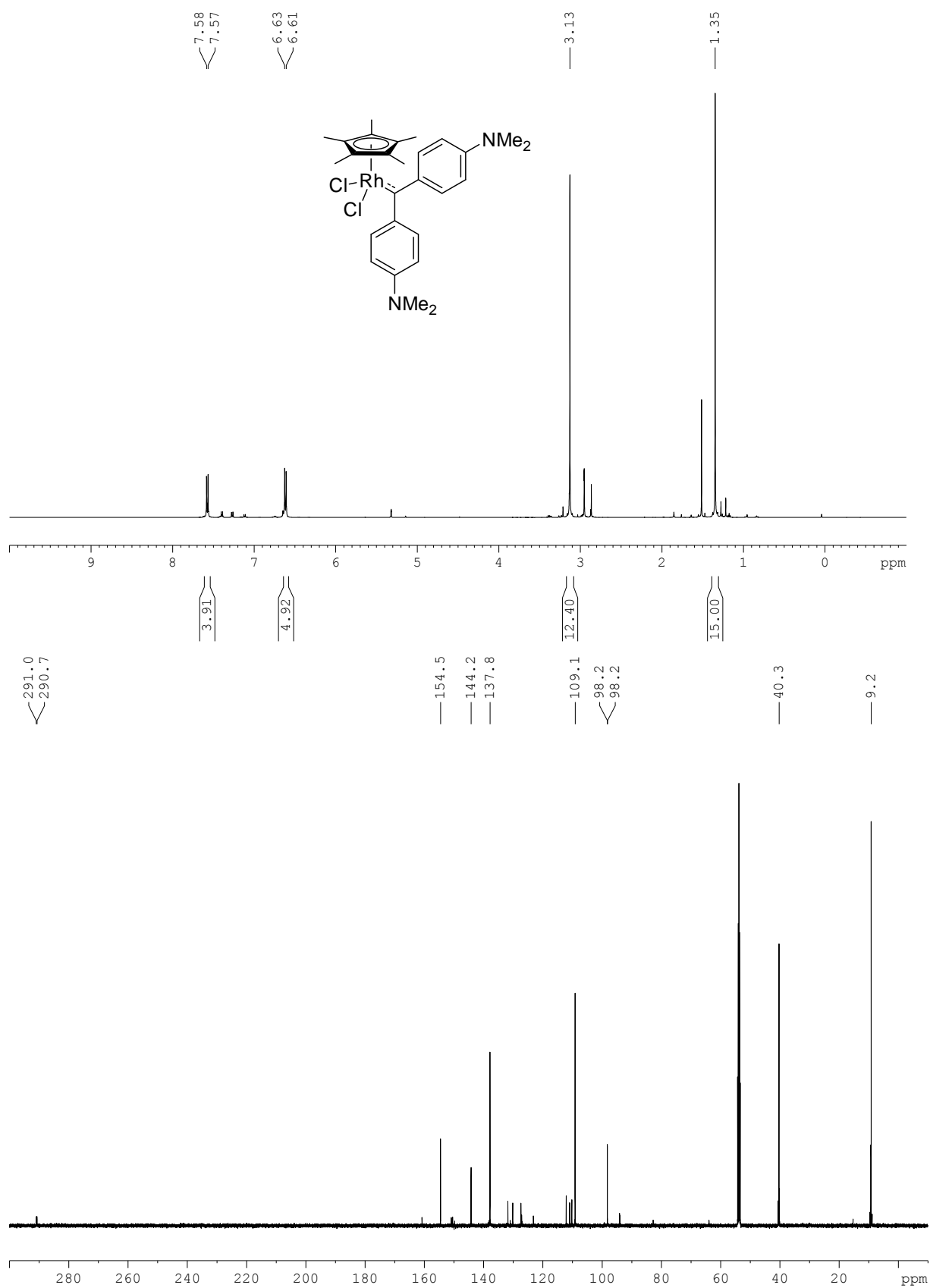
# Iridium Carbene Complex 14b



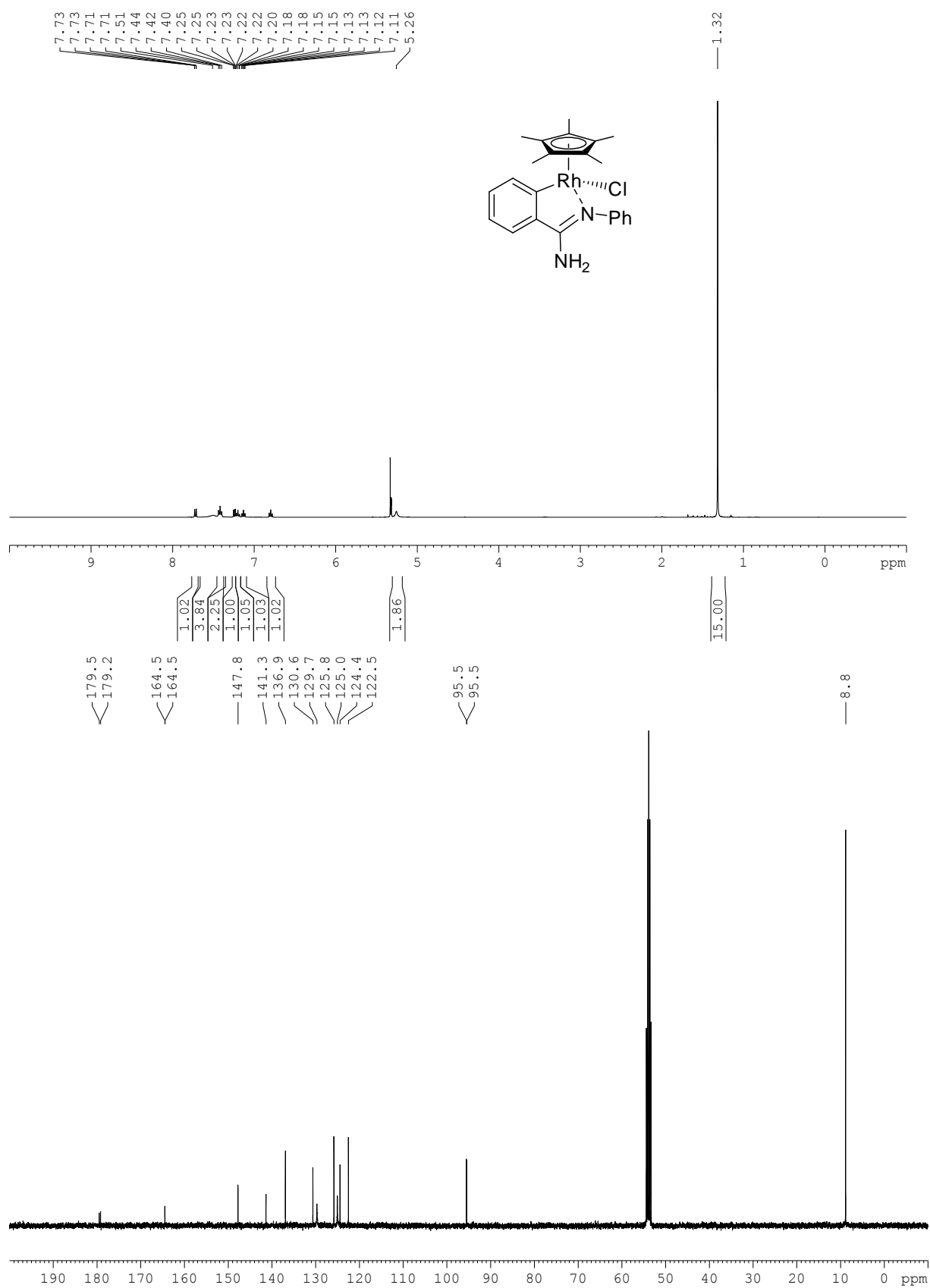
# Iridium Carbene Complex 15



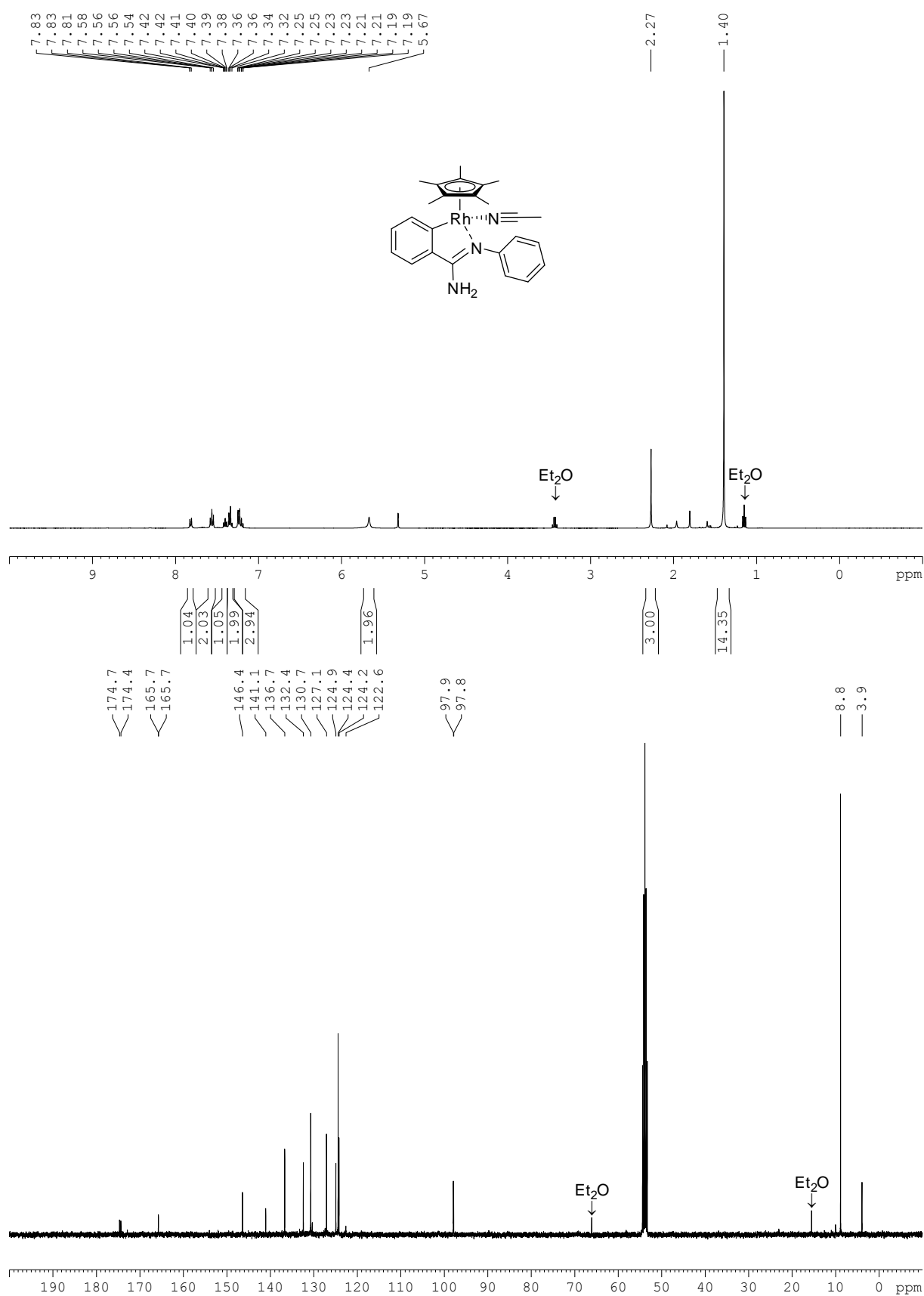
# Rhodium Carbene Complex 12



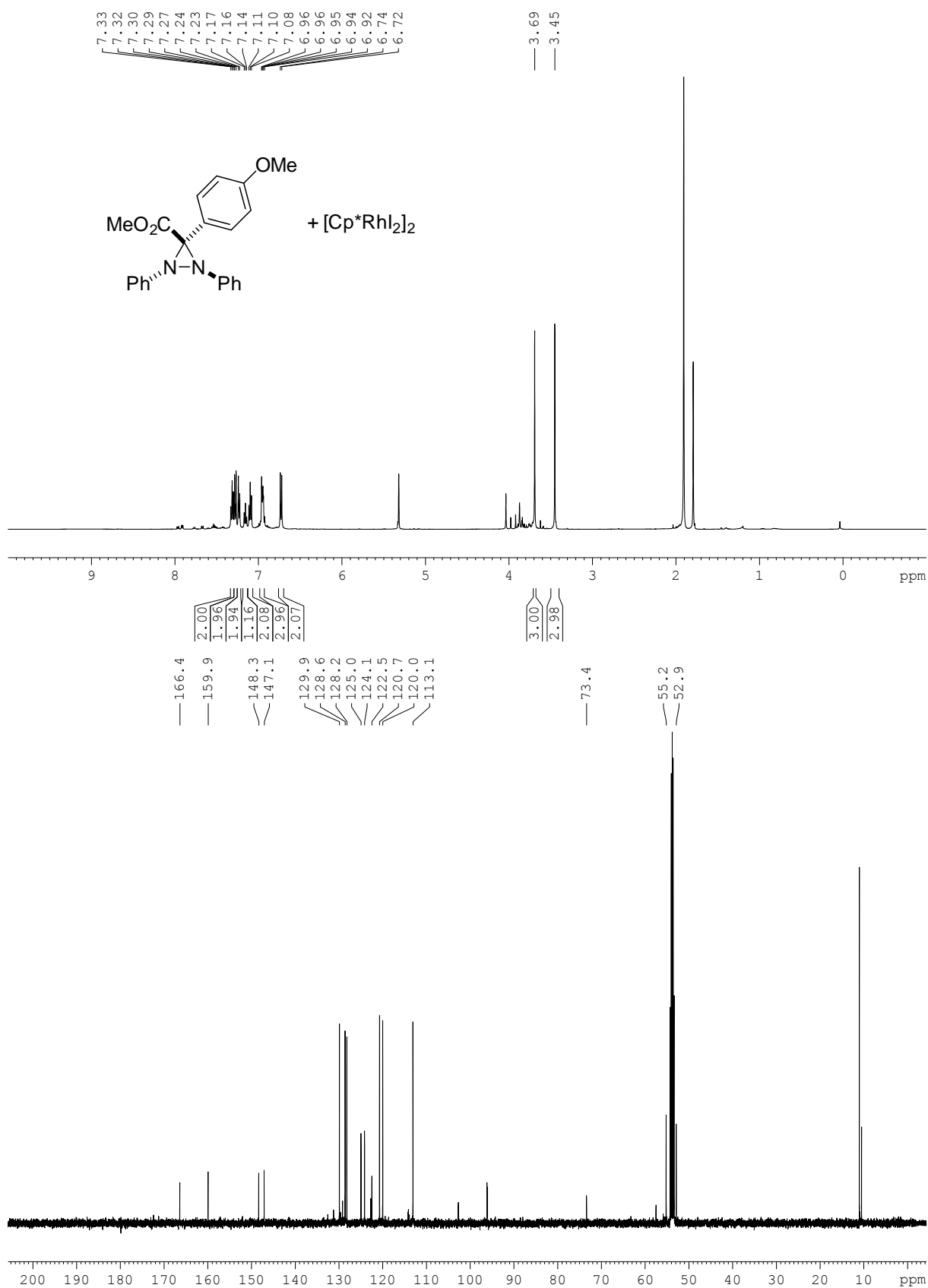
### Cyclometalated Complex 4



### Cyclometallated acetonitrile complex 2

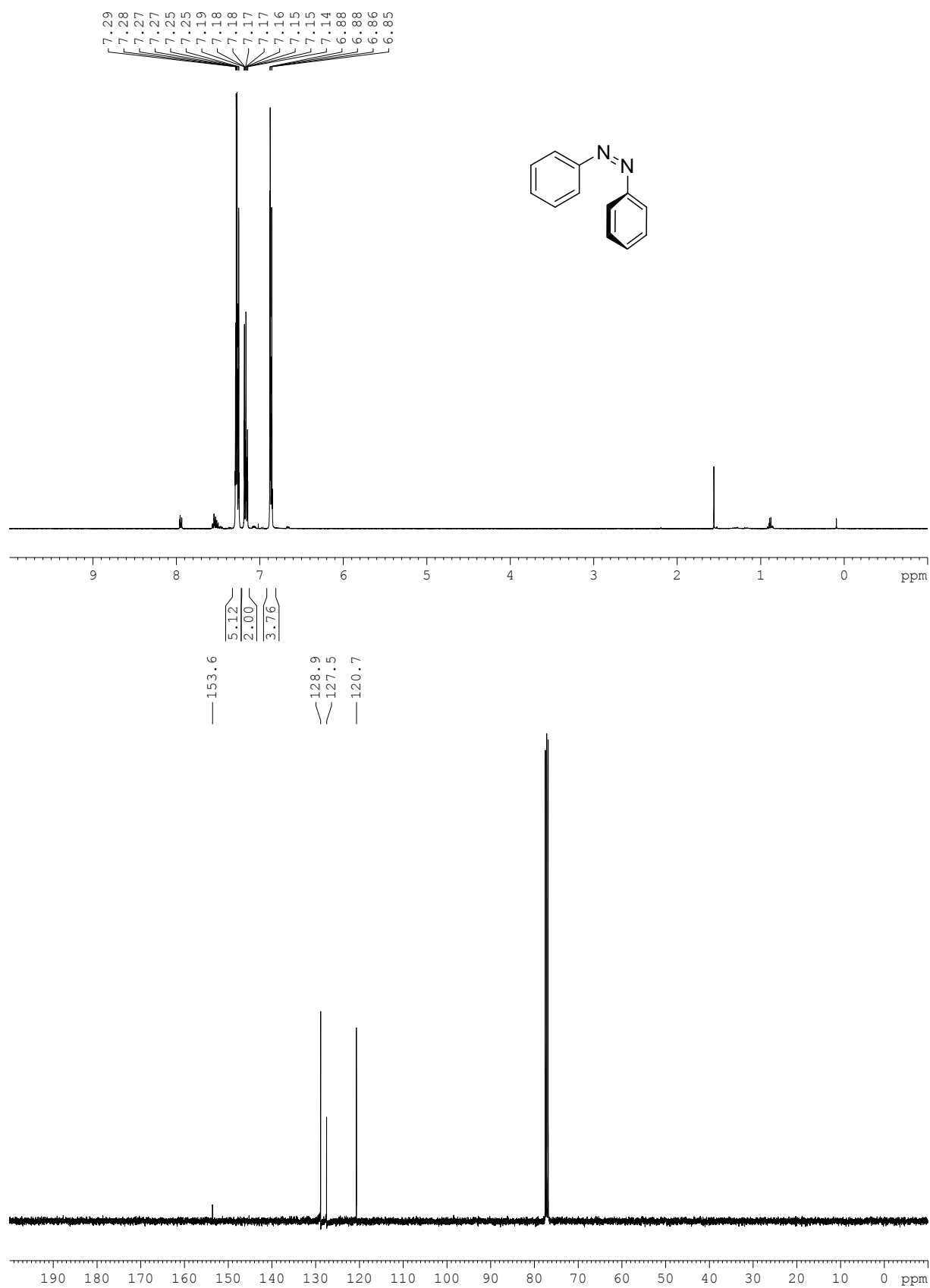


# Diaziridine 41

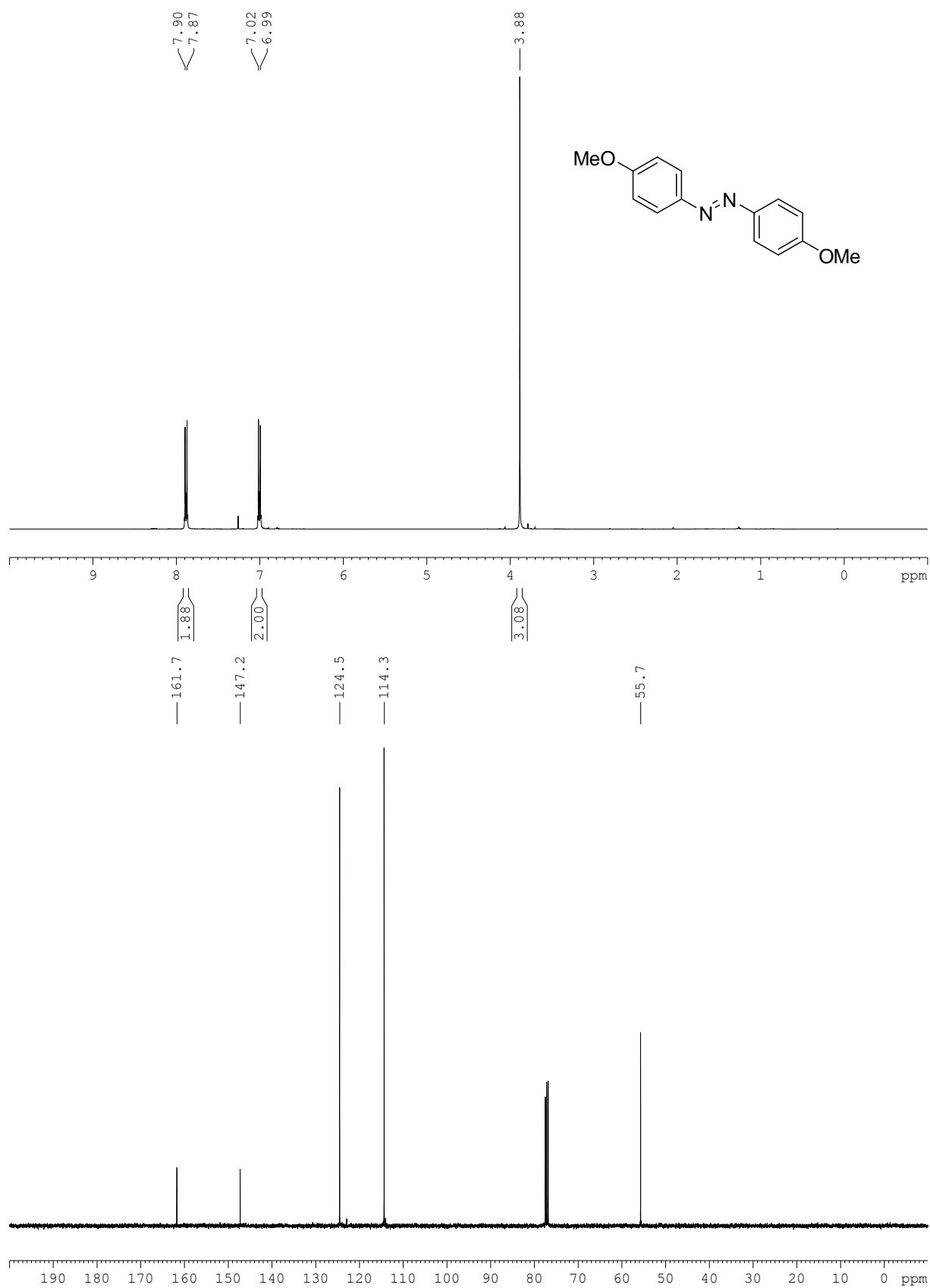




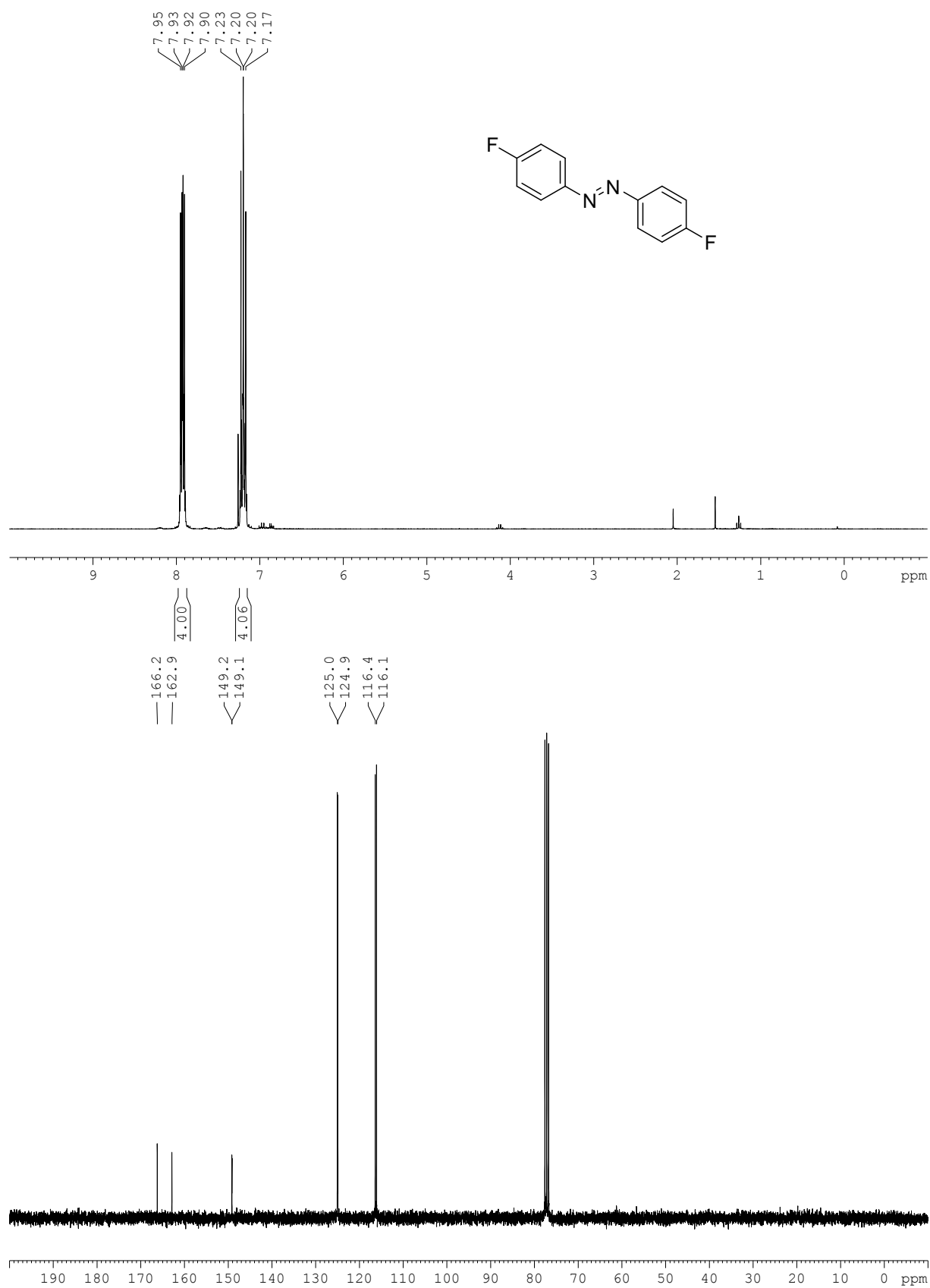
Compound (Z)-16



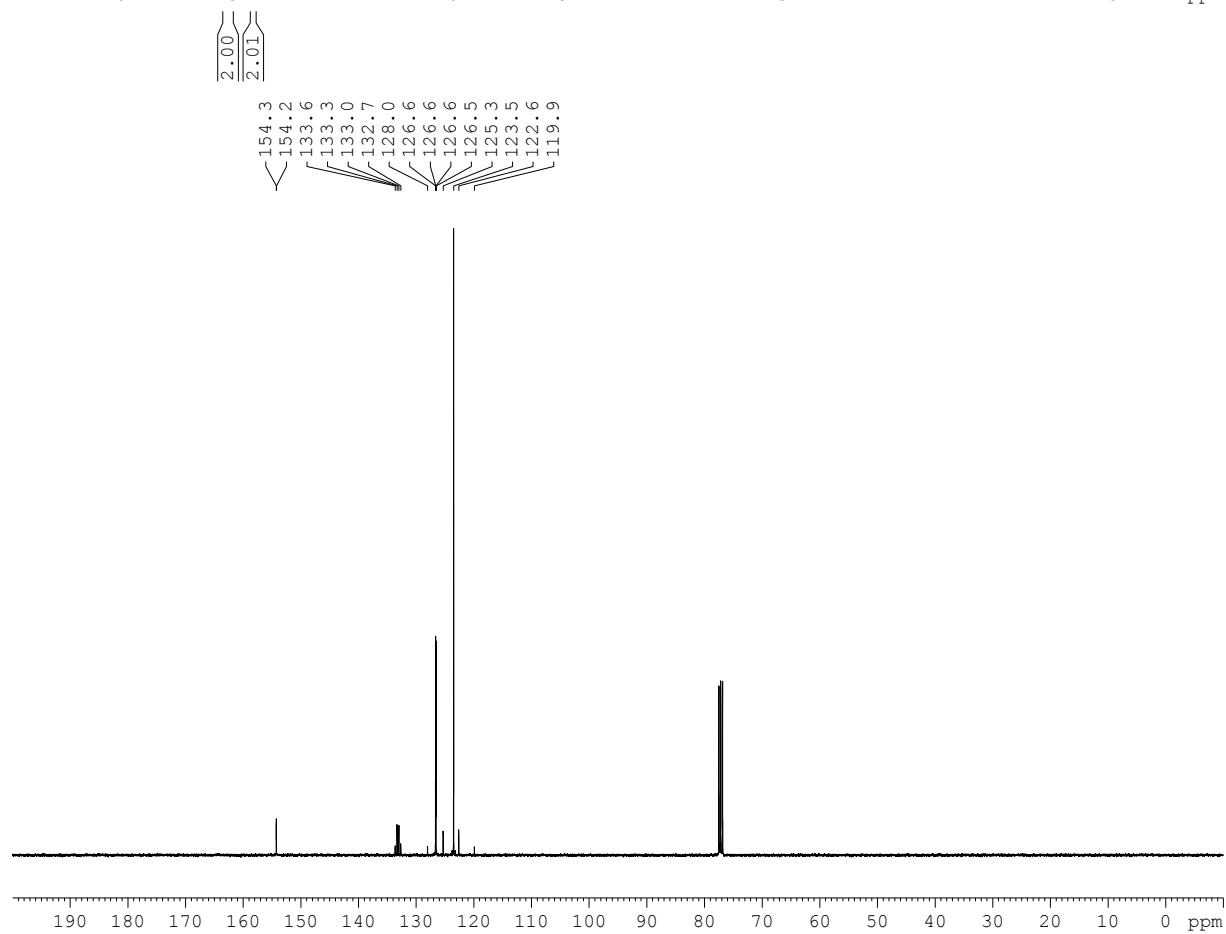
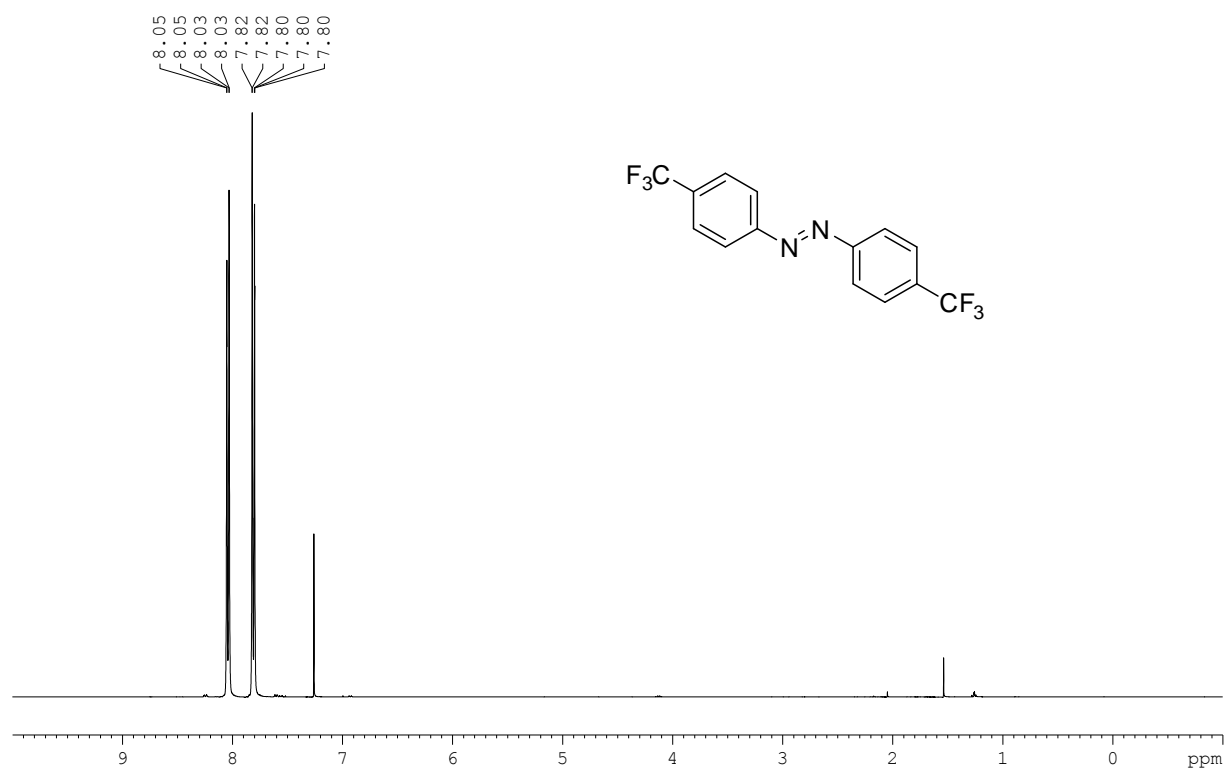
**(E)-1,2-Bis(4-methoxyphenyl)diazene**



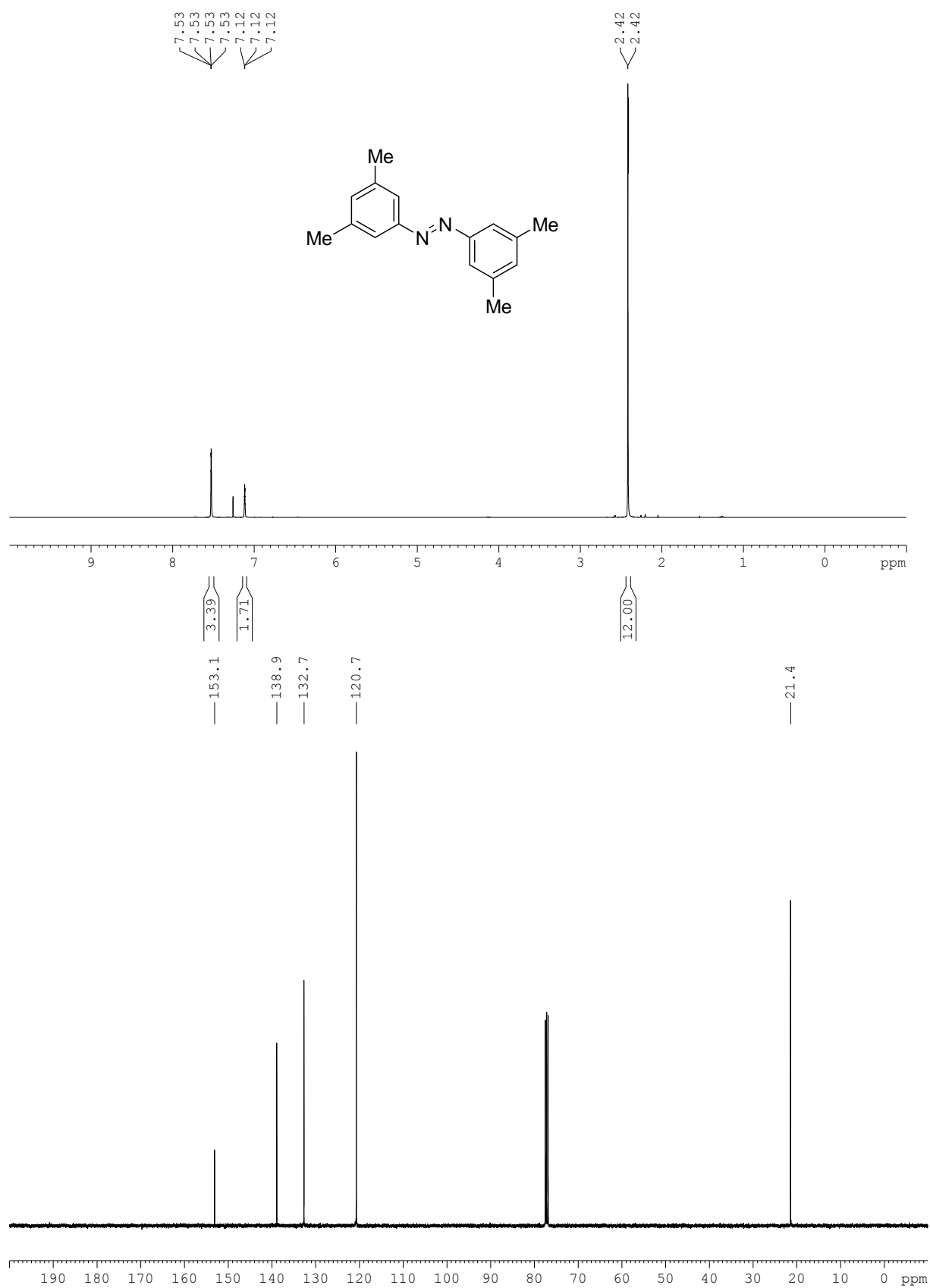
**(E)-1,2-Bis(4-fluorophenyl)diazene**



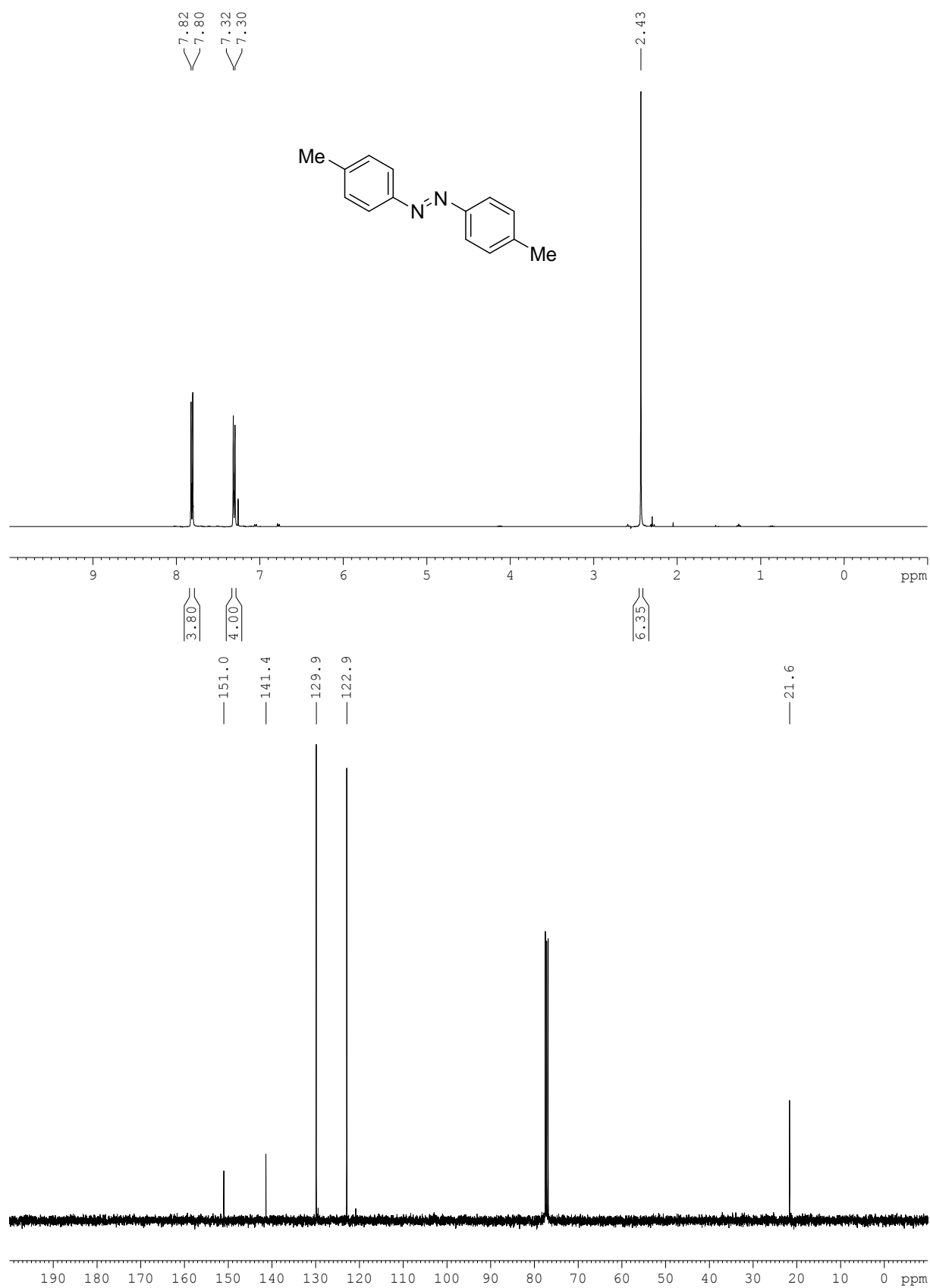
**(E)-1,2-Bis(4-(trifluoro-methyl)phenyl)diazene**



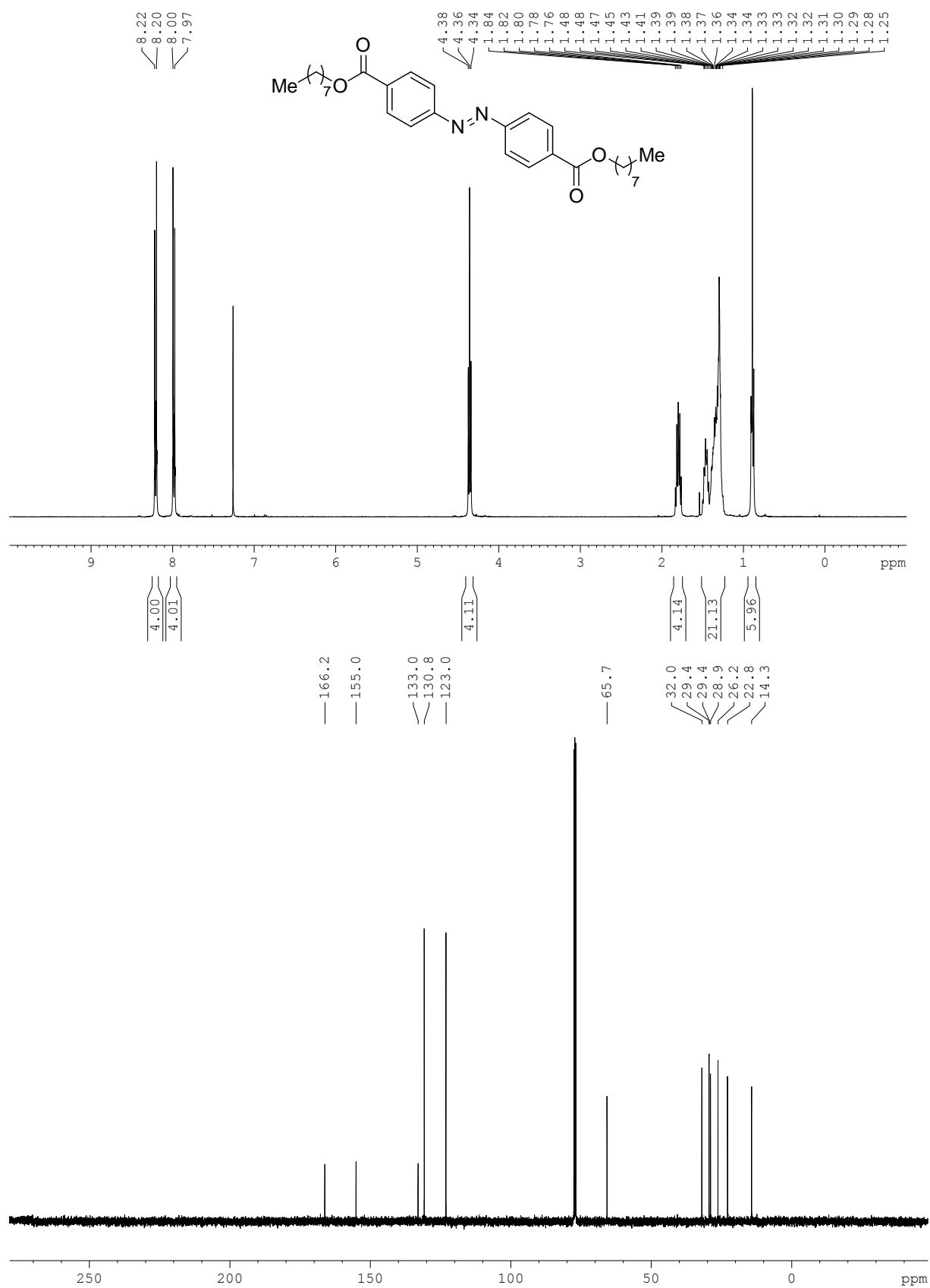
**(E)-1,2-Bis(3,5-dimethylphenyl)diazene**



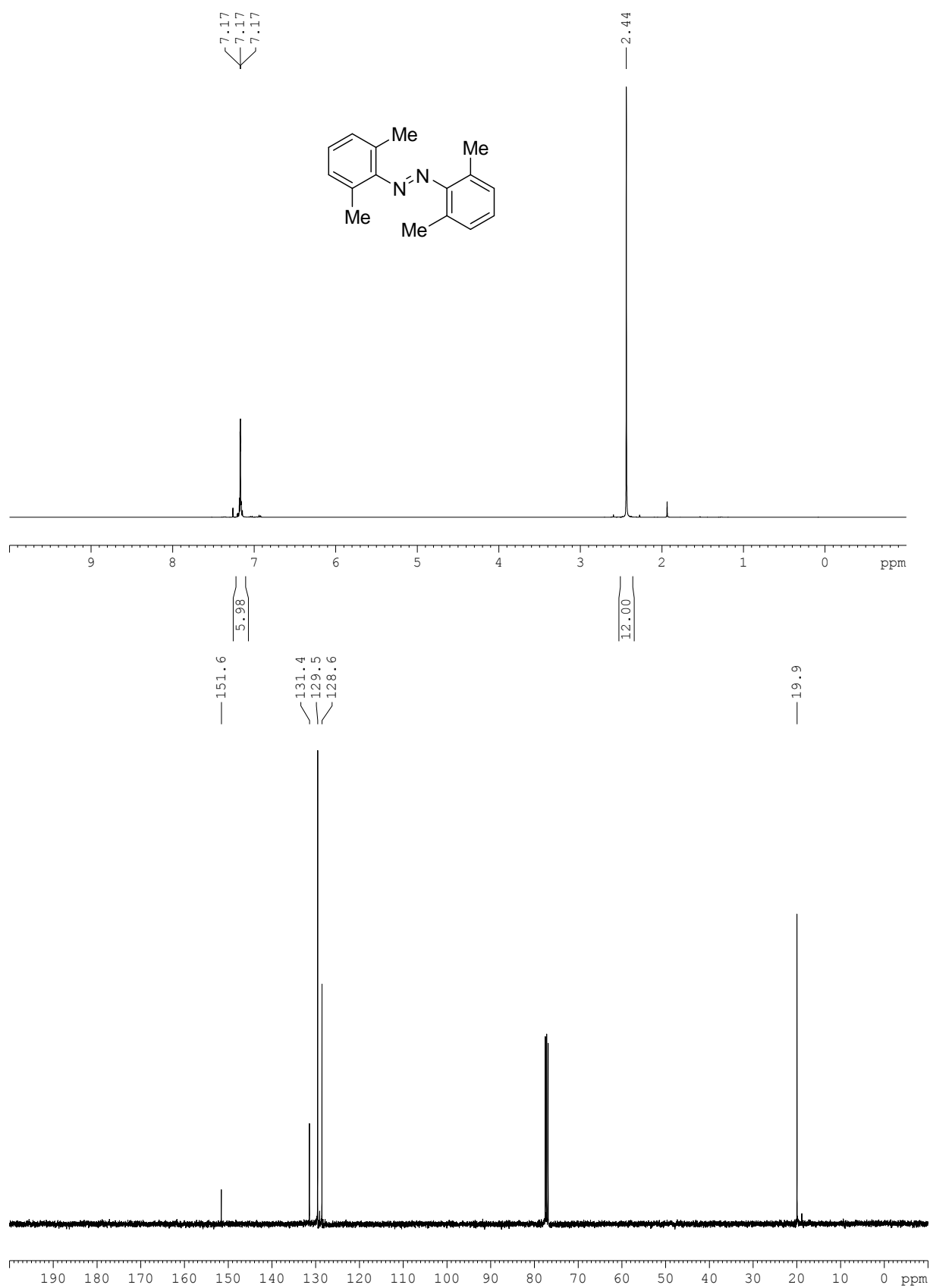
**(E)-1,2-Di-p-tolyldiazene**



**Diocyl 4,4'-(diazene-1,2-diyl)(E)-dibenzoate**

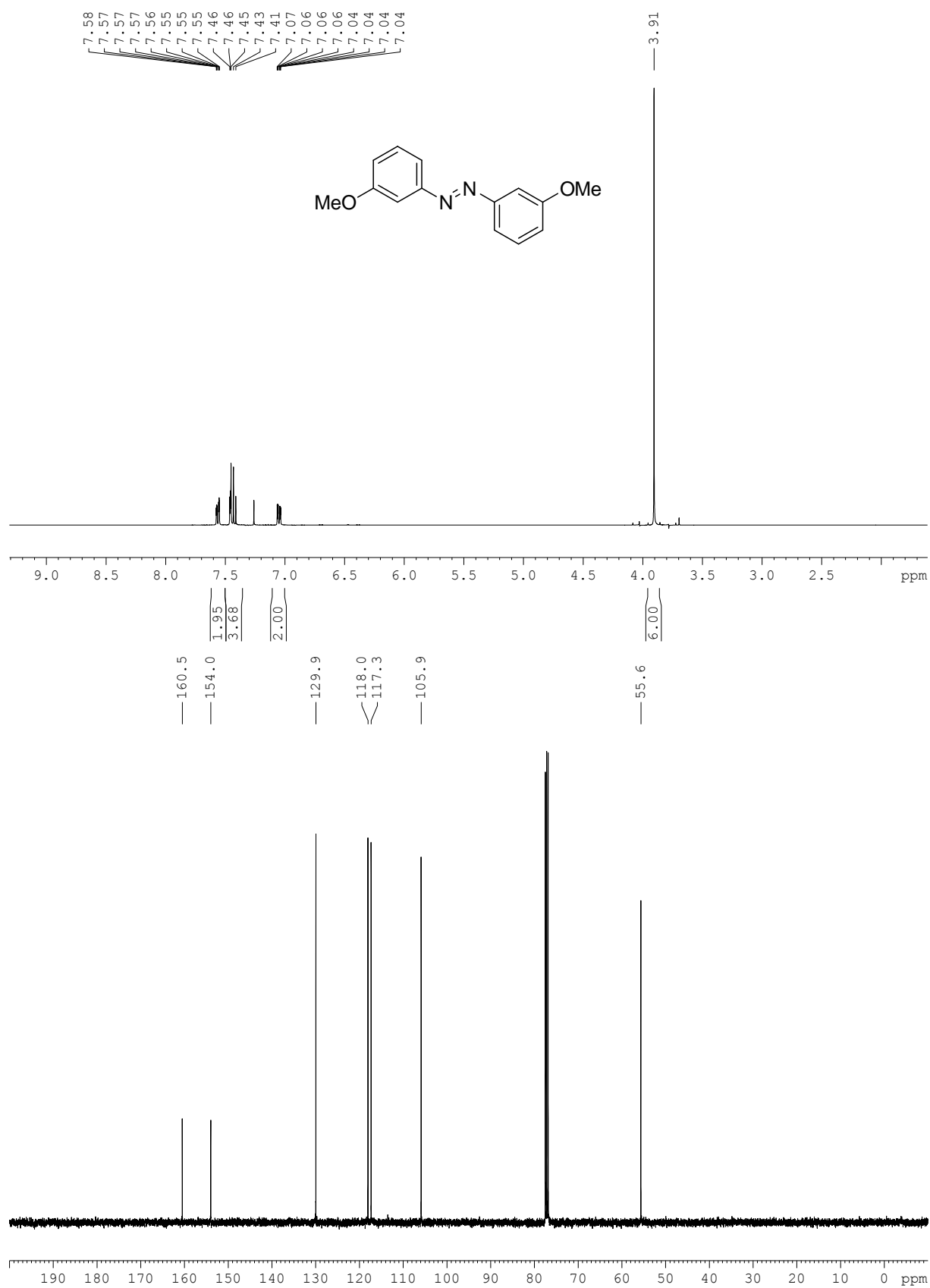


**(E)-1,2-Bis(2,6-dimethylphenyl)diazene**





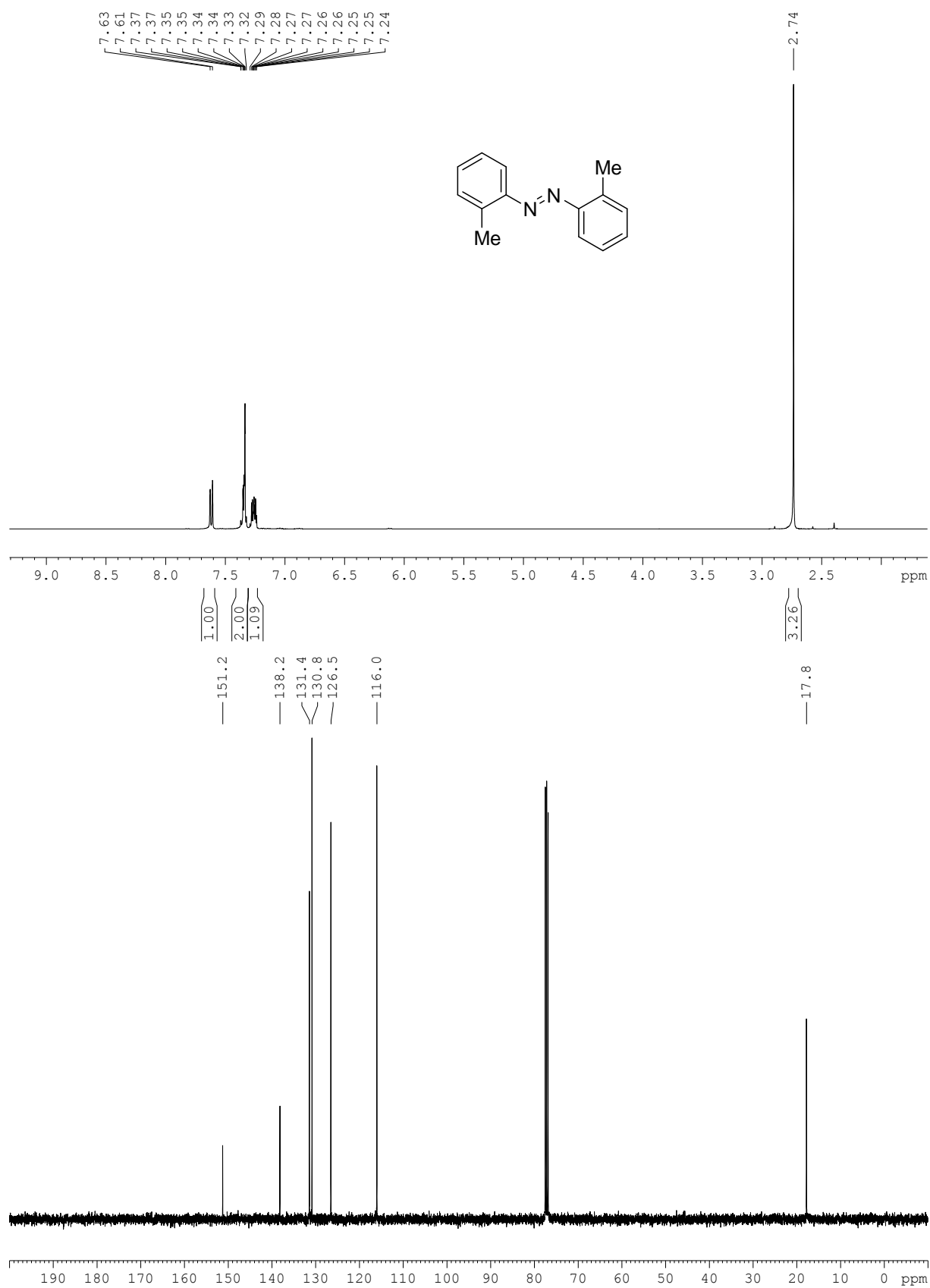
**(E)-1,2-Bis(3-methoxyphenyl)diazene**



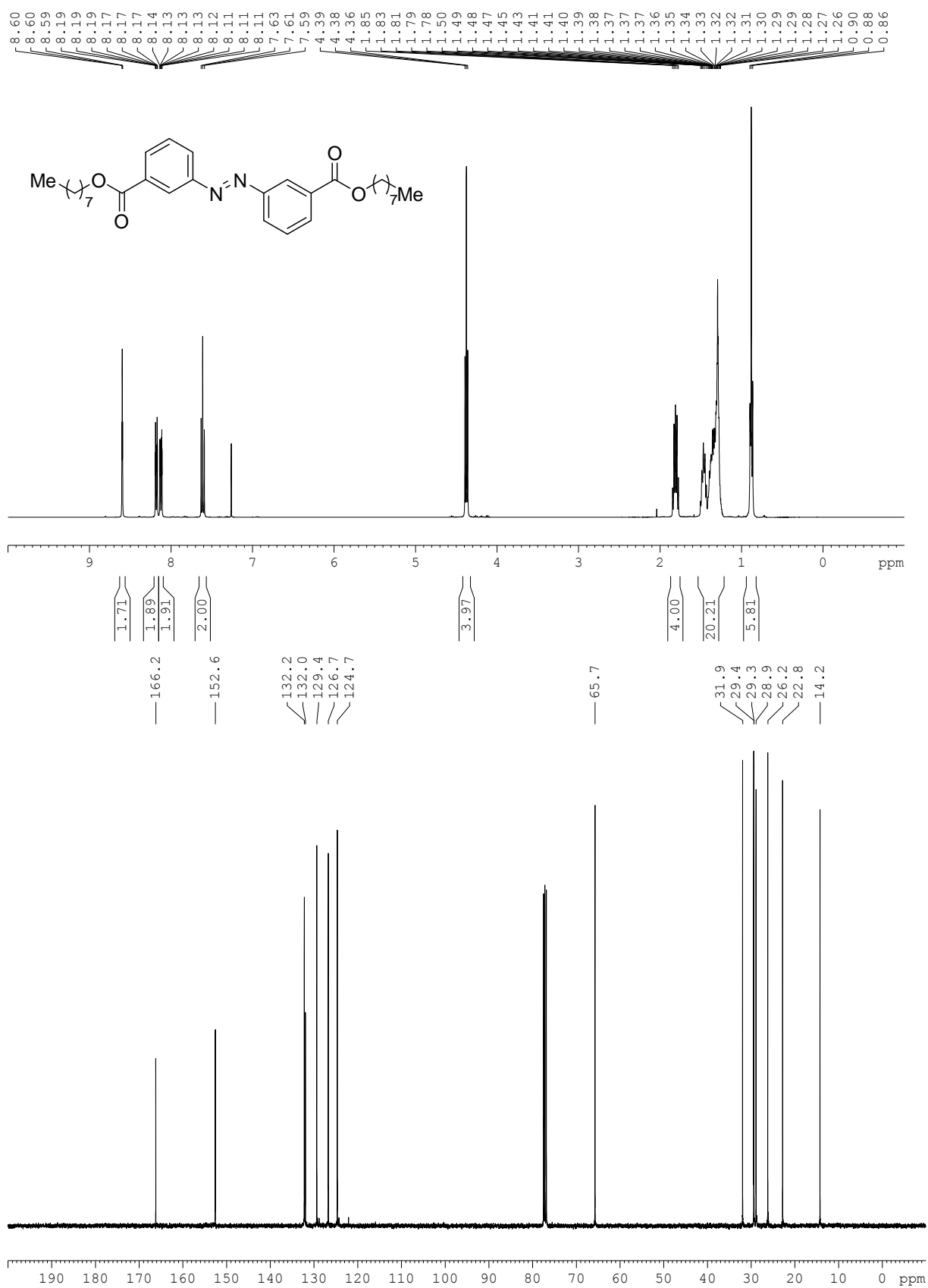
**(E)-1-(p-Tolyl)-2-(4-(trifluoromethyl)phenyl)diazene**



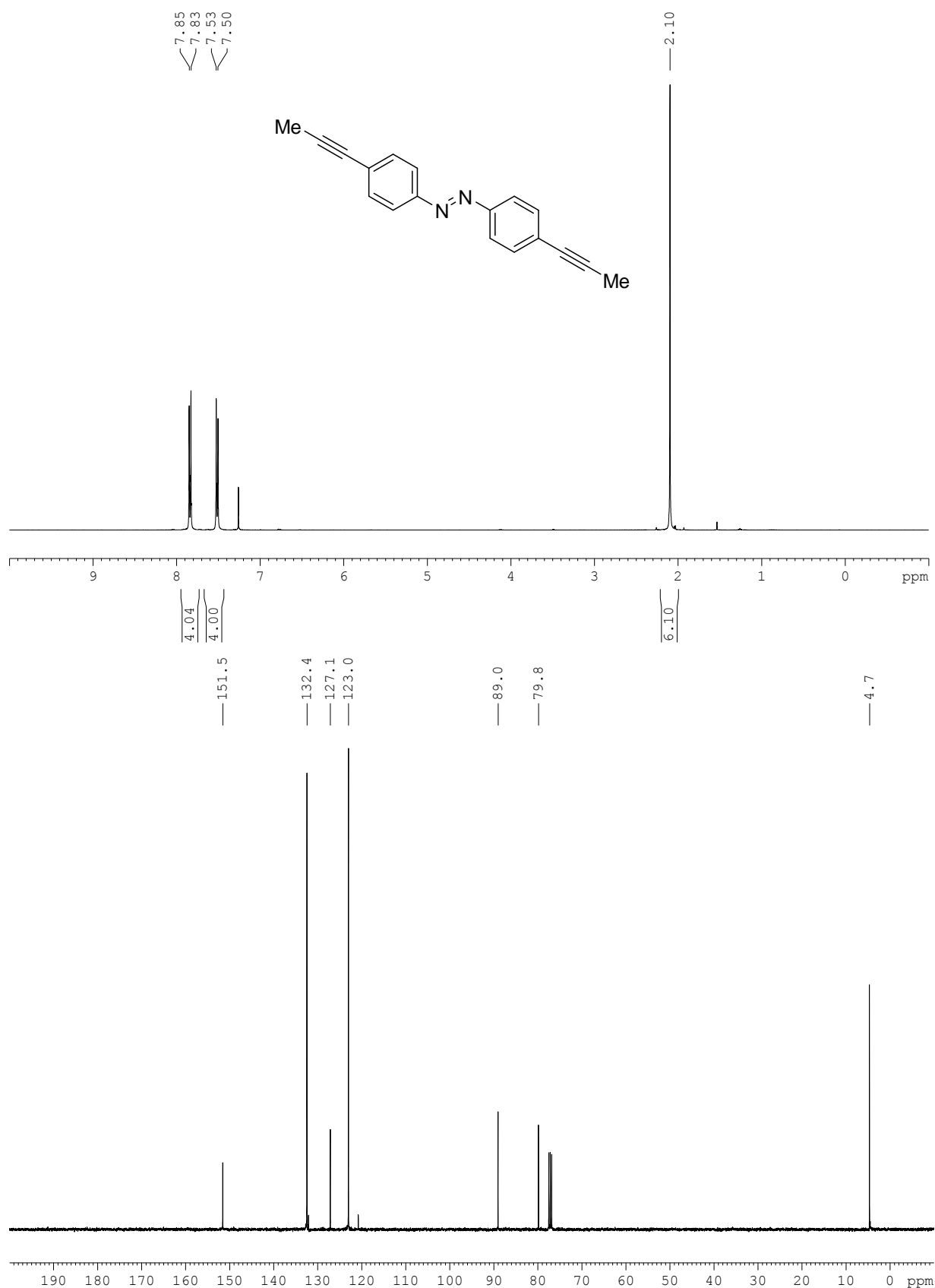
**(E)-1,2-Di-o-tolyl-diazene**



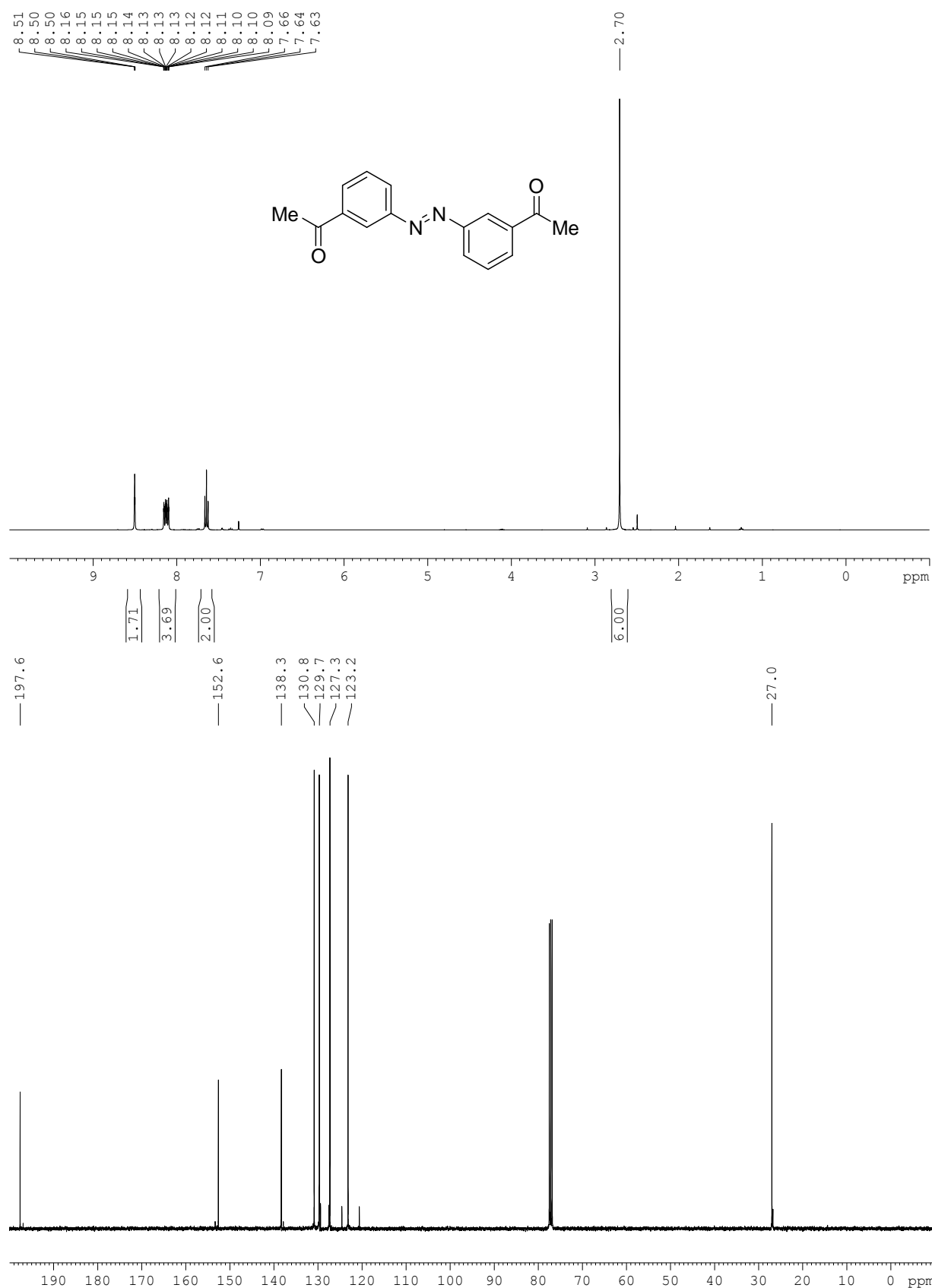
**Diocyl 3,3'-(diazene-1,2-diyl)(E)-dibenzoate**



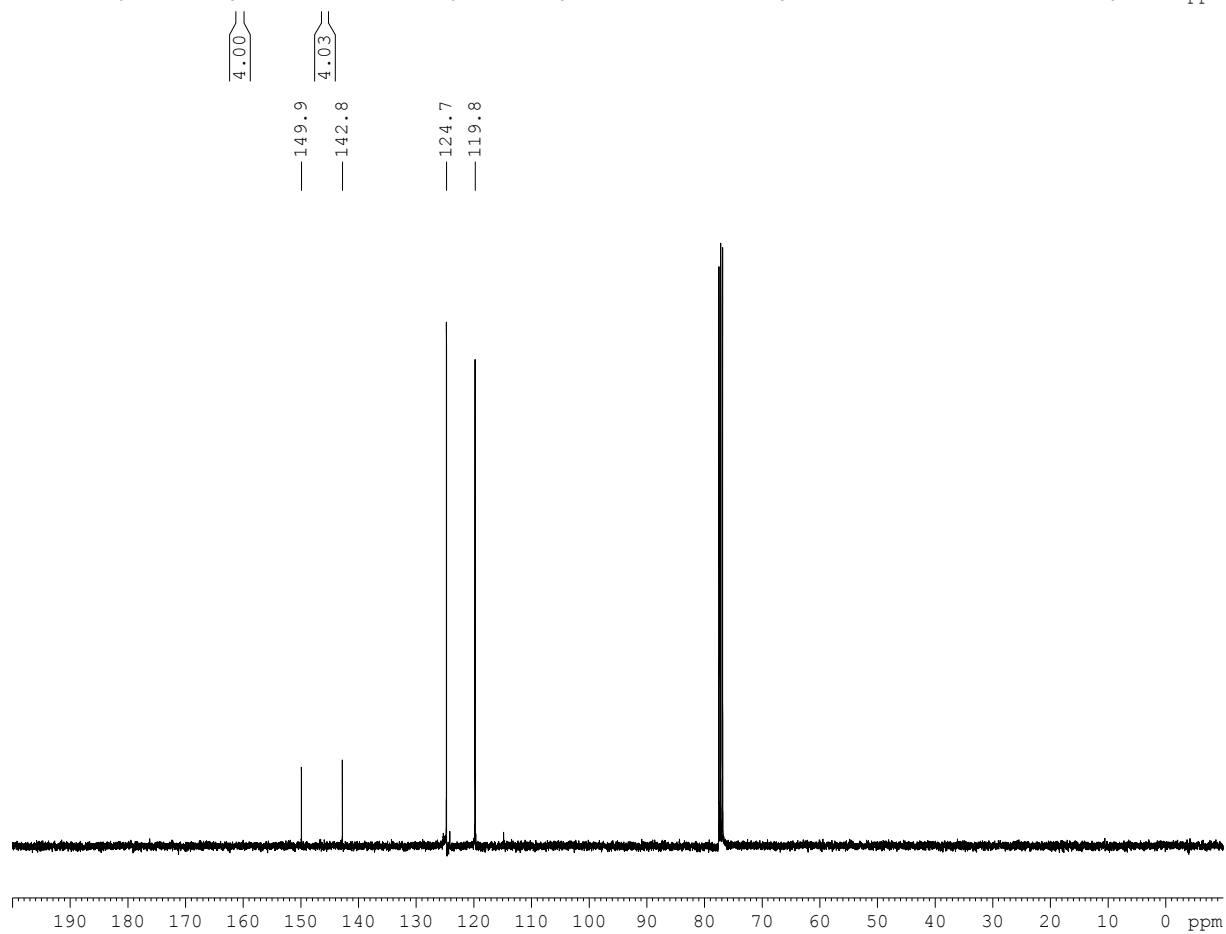
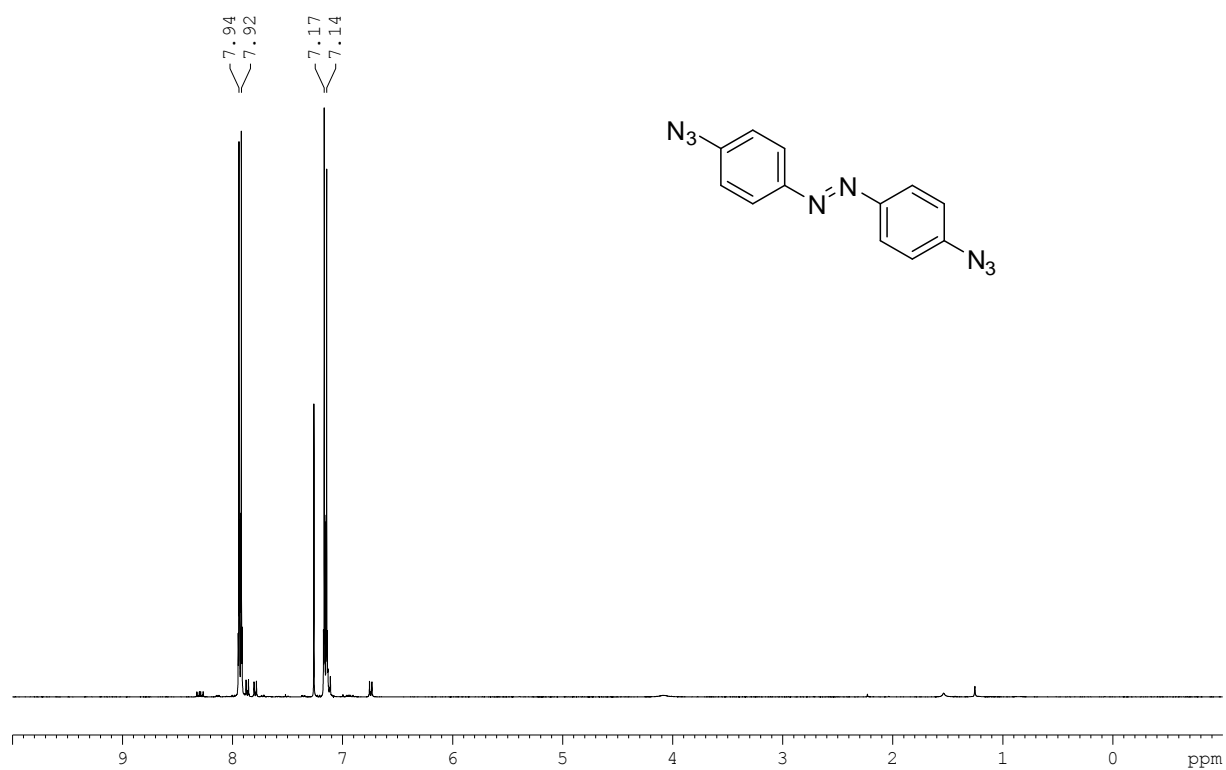
**(E)-1,2-Bis(4-(prop-1-yn-1-yl)phenyl)diazene**



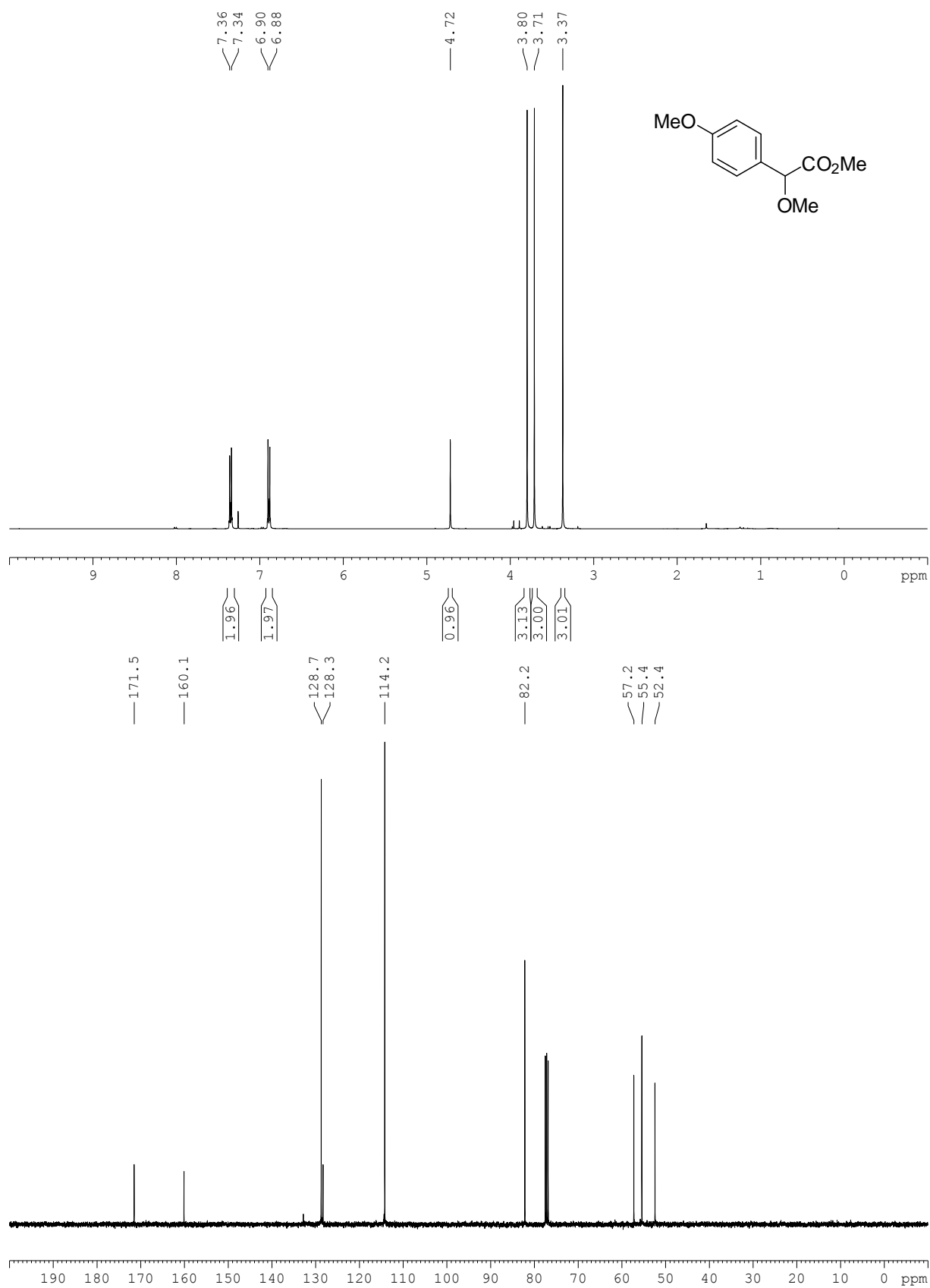
**(E)-1,1'-(Diazene-1,2-diylbis(3,1-phenylene))bis(ethan-1-one)**



**(E)-1,2-Bis(4-azido-phenyl)diazene**

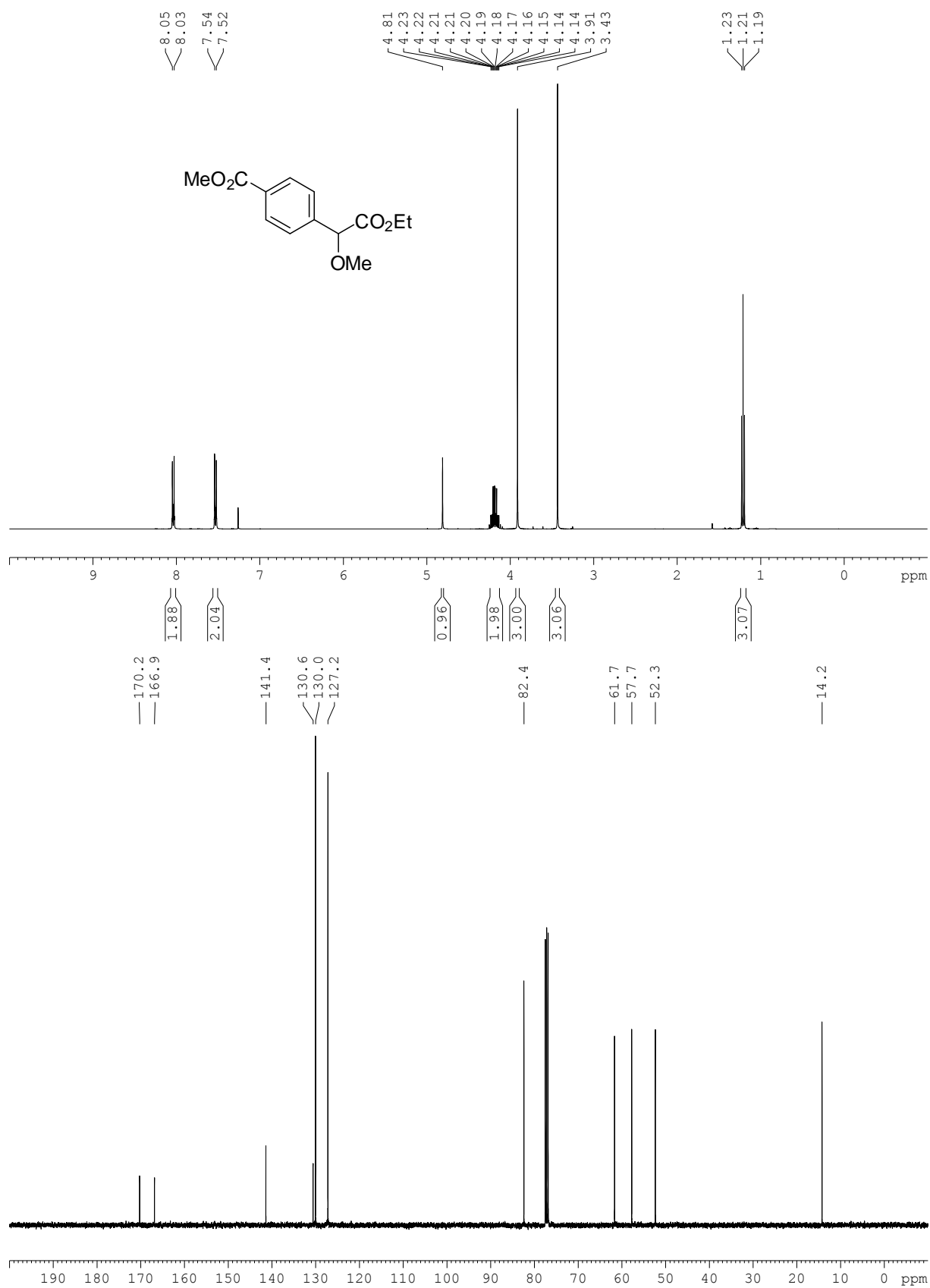


# Compound 9a

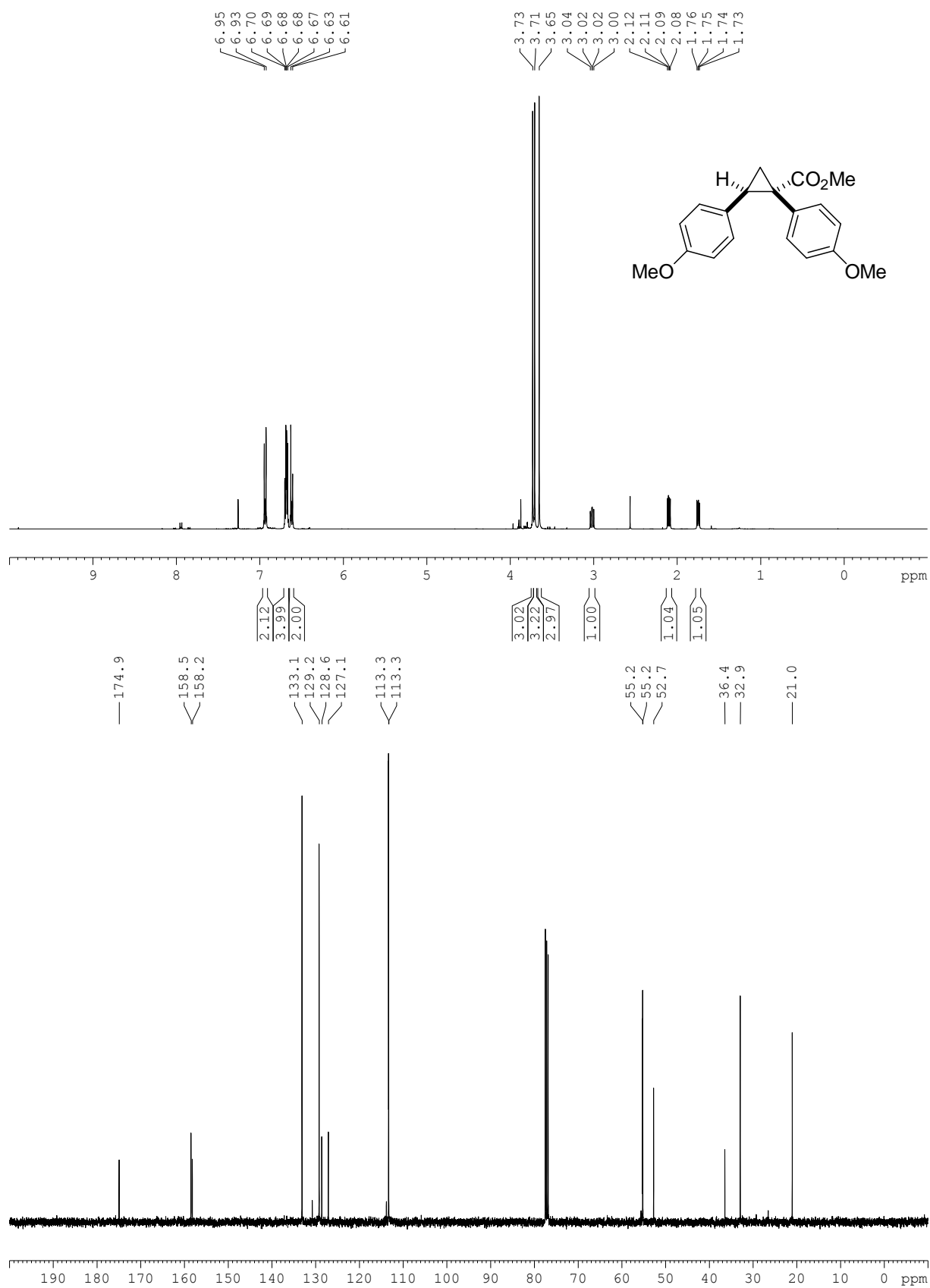




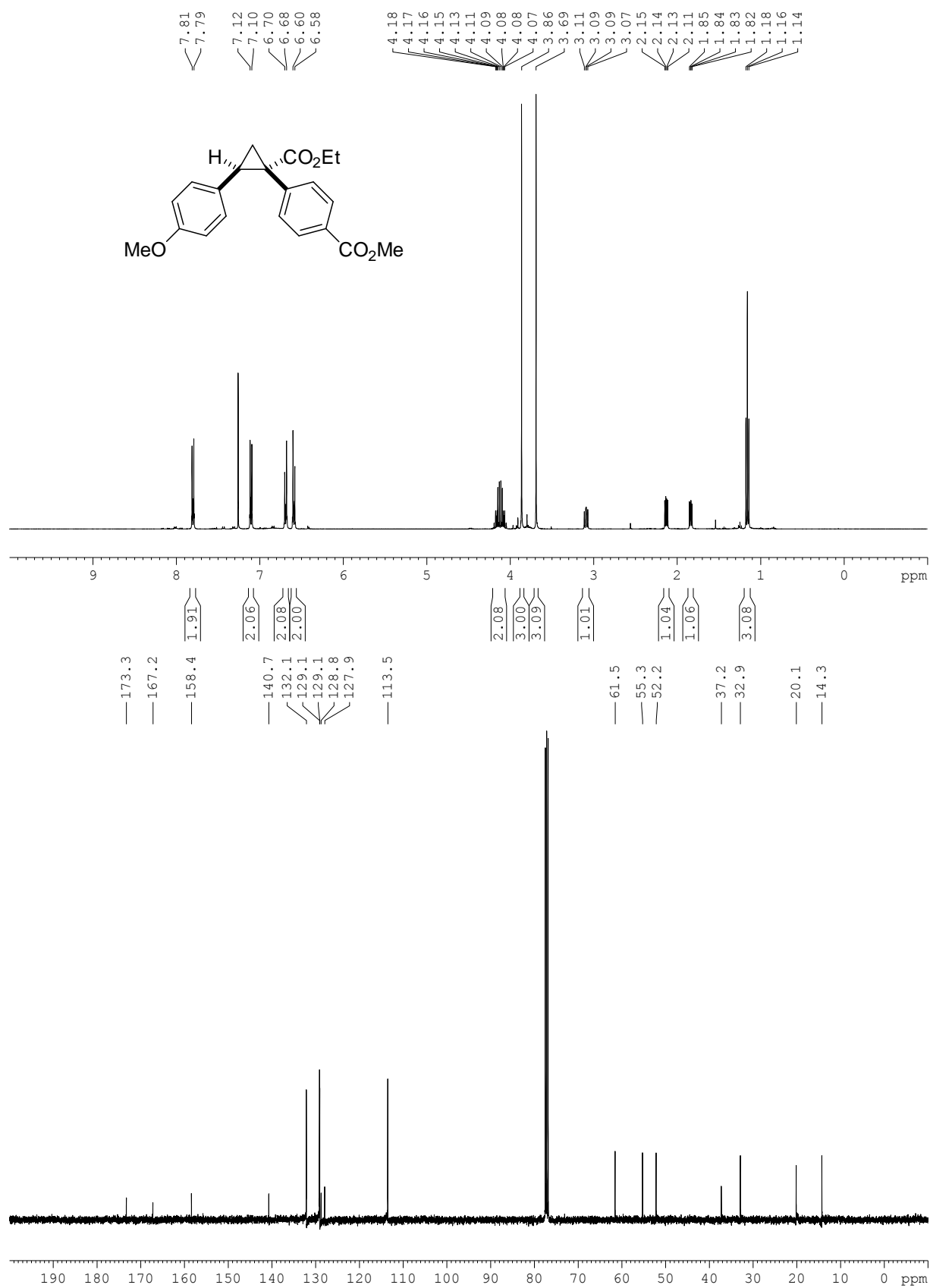
# Compound 9b



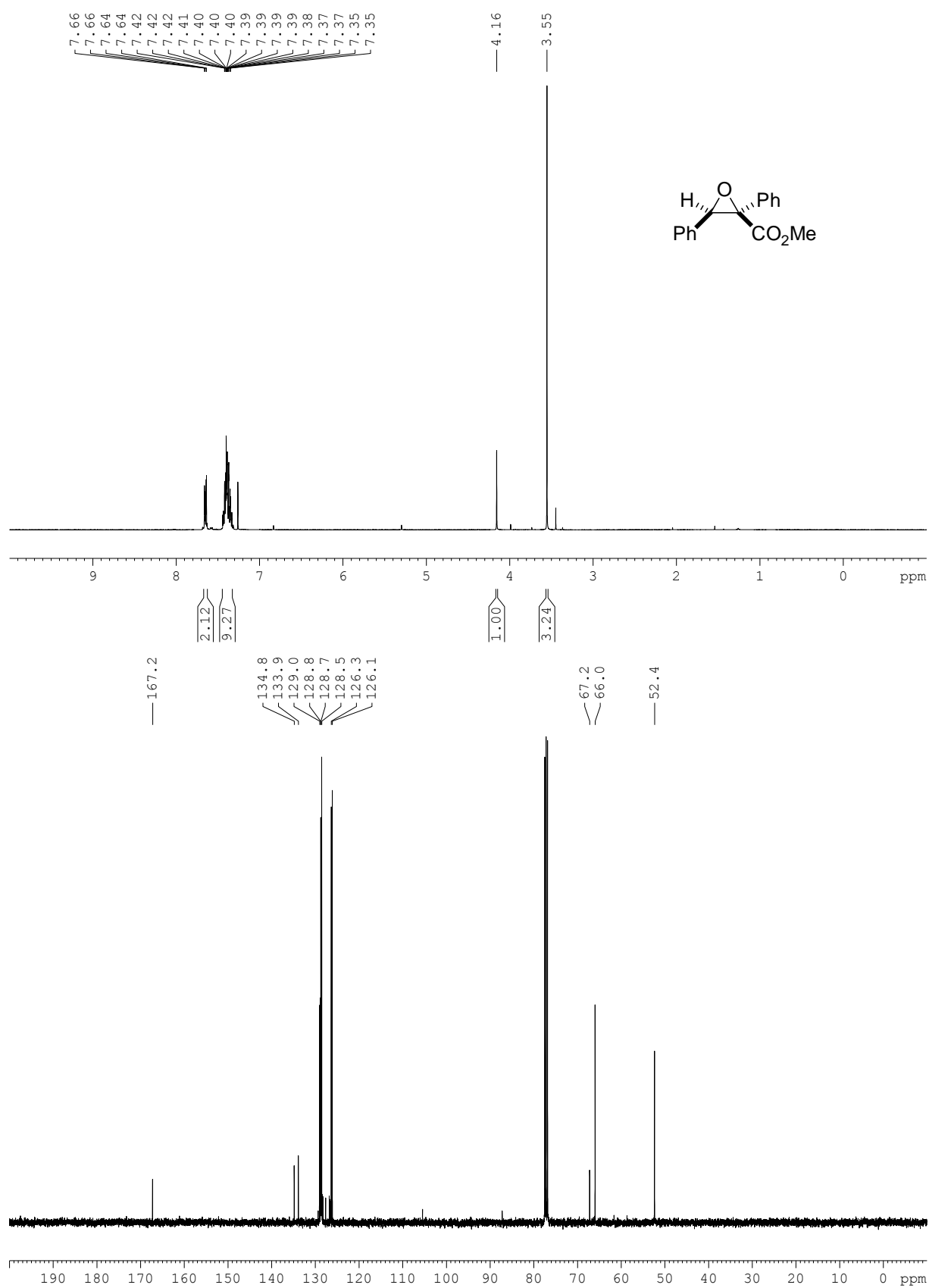
Compound 7a



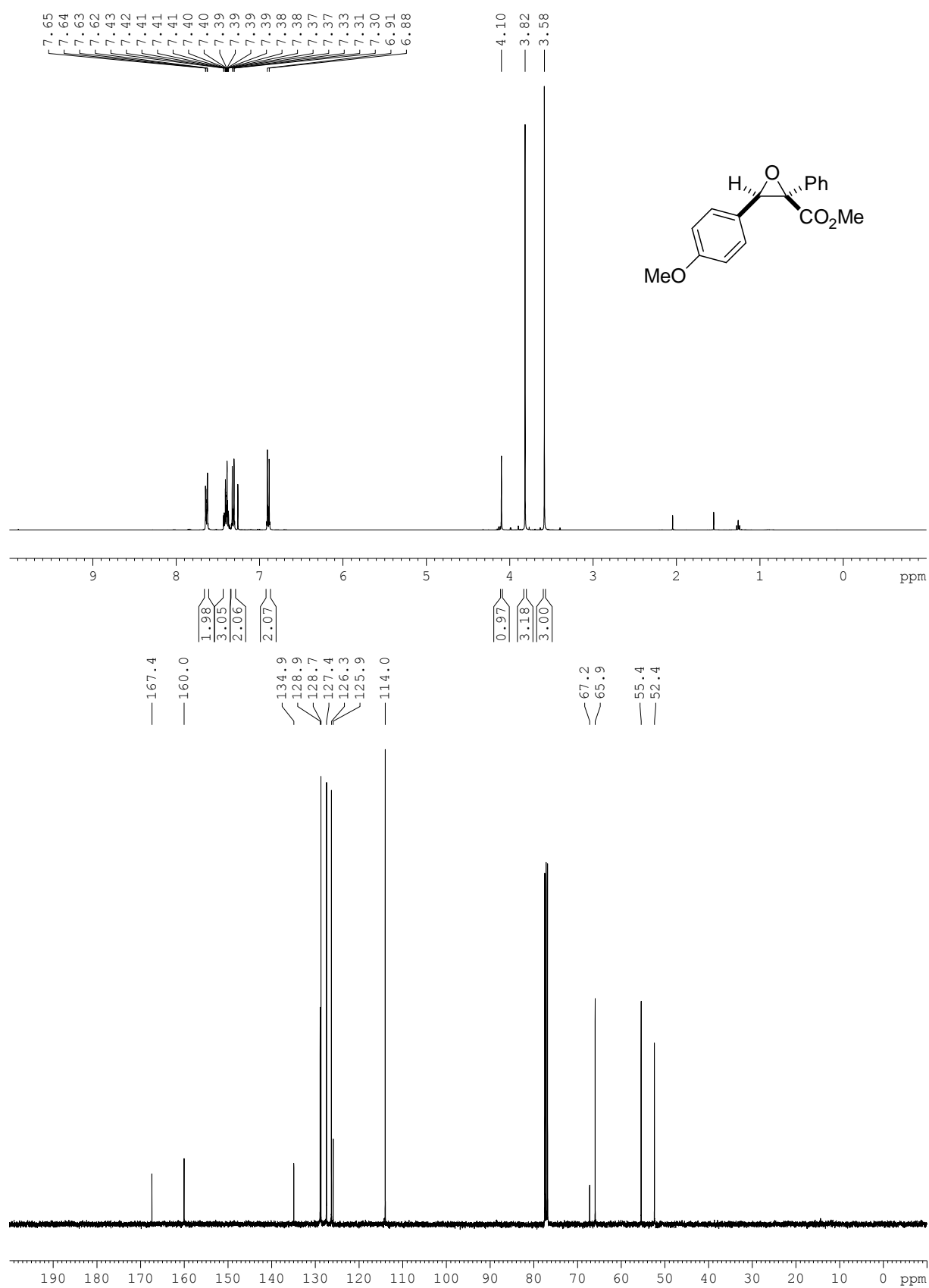
**Compound 7b**



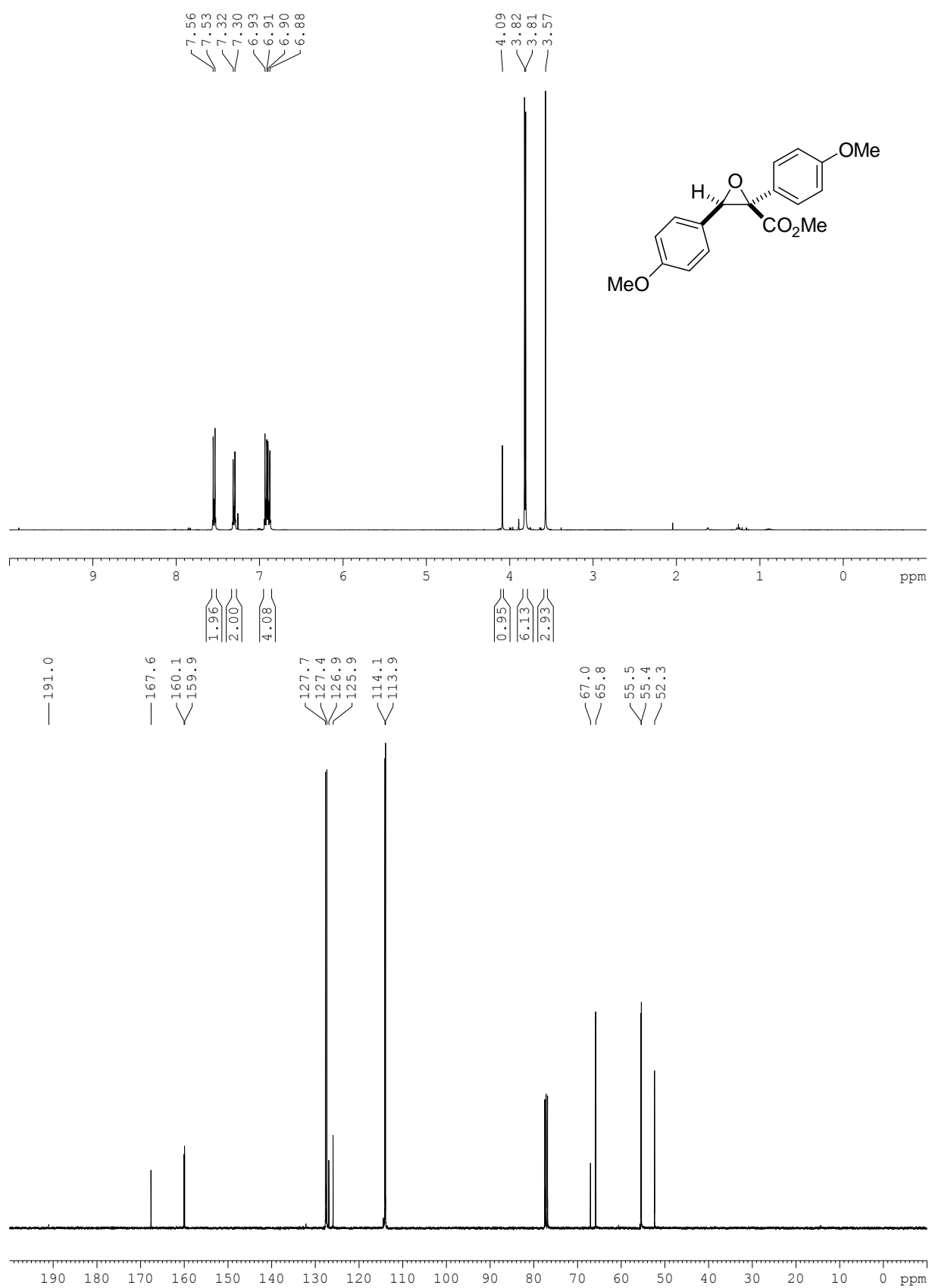
Compound from table 2, entry 1



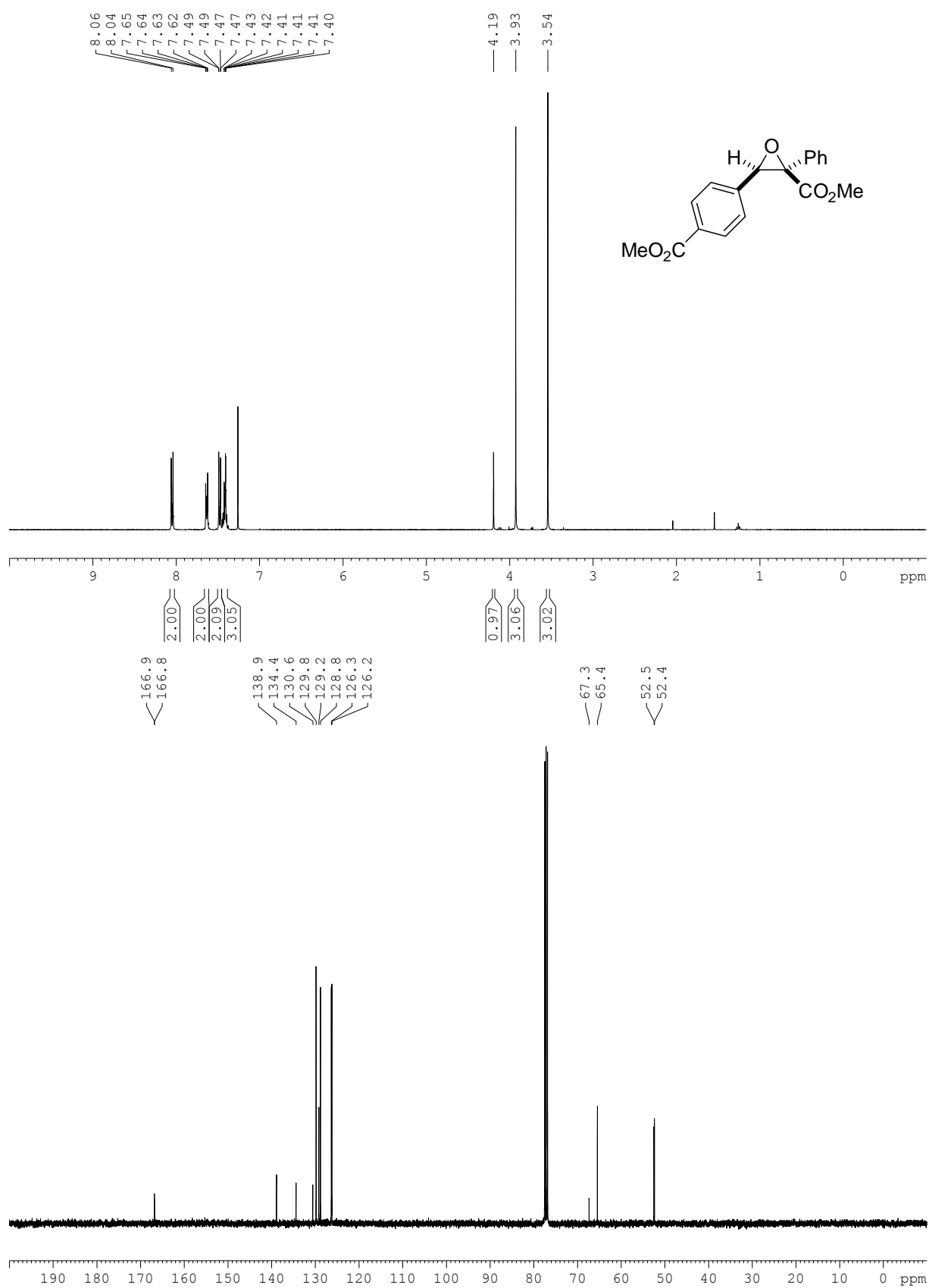
Compound from table 2, entry 4



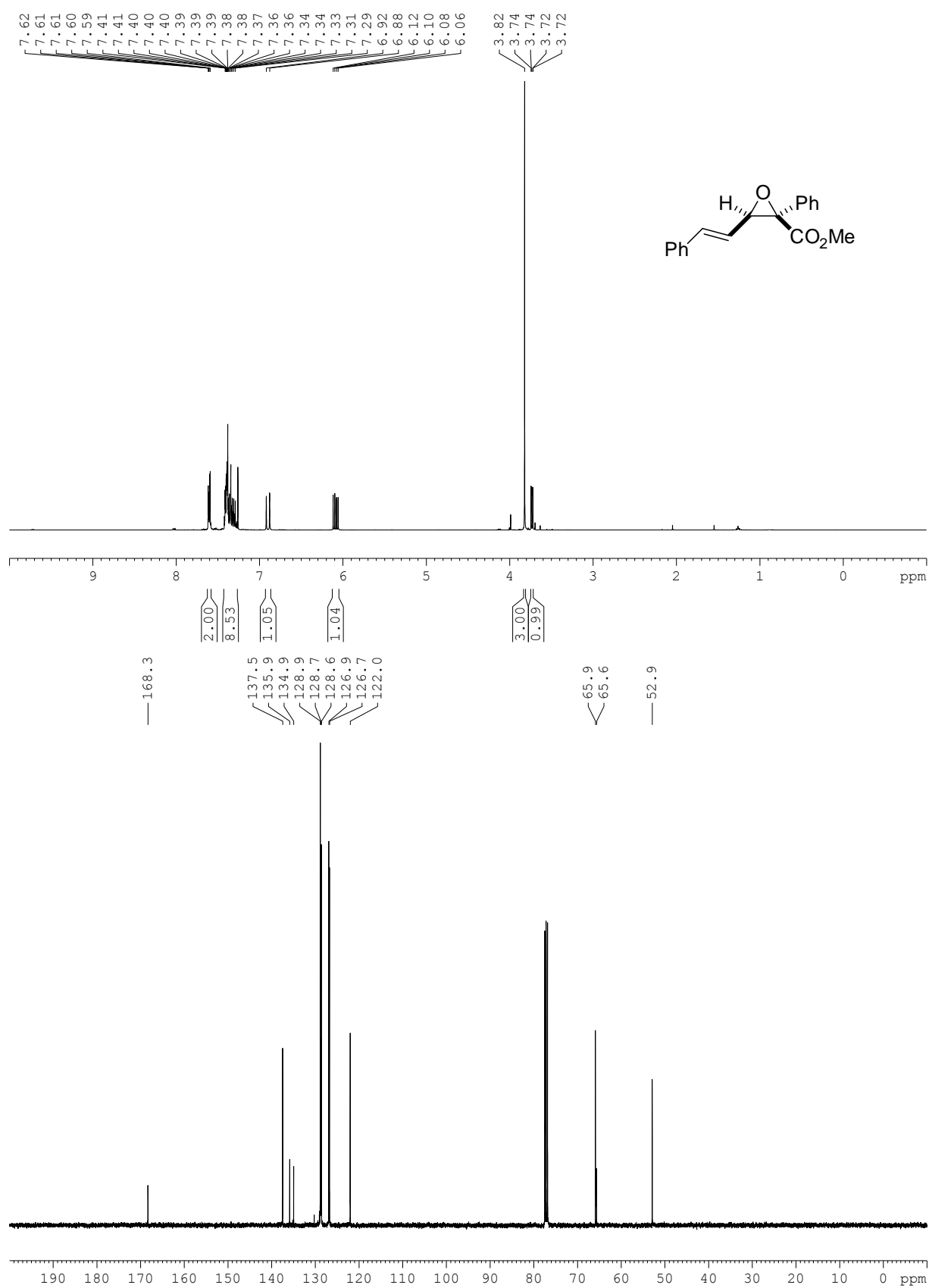
Compound from table 2, entry 5



Compound from table 2, entry 6

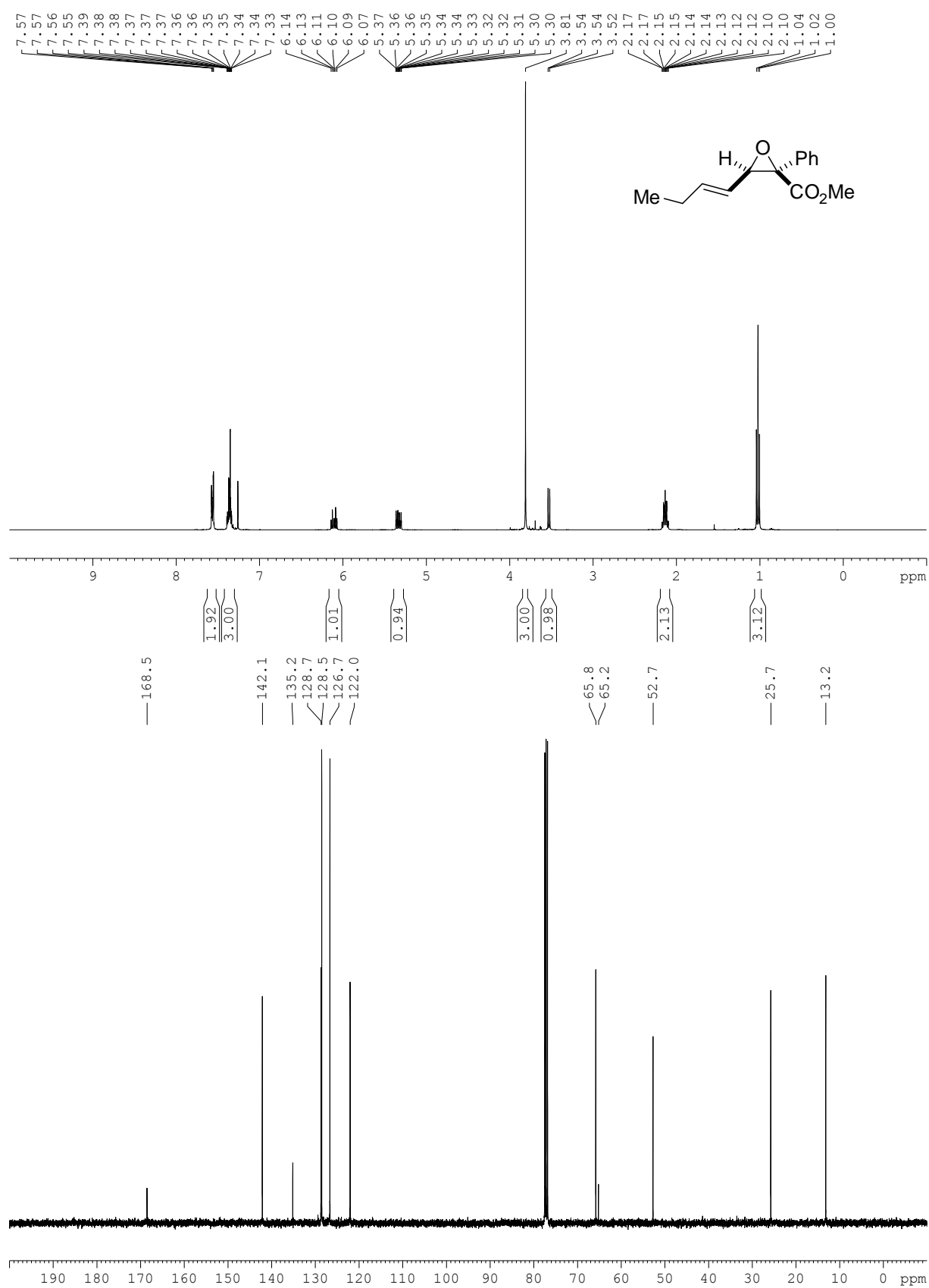


Compound from table 2, entry 7

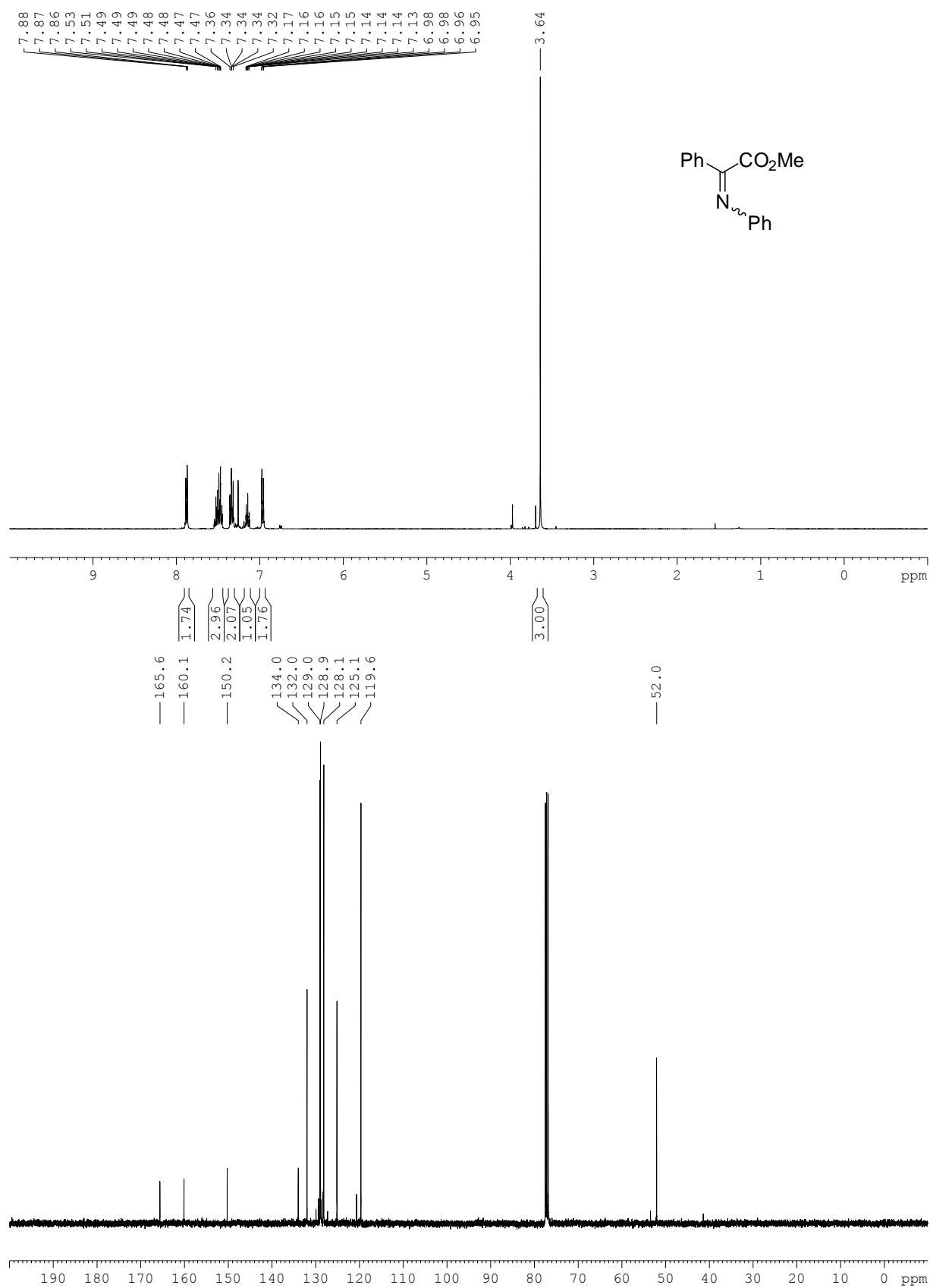




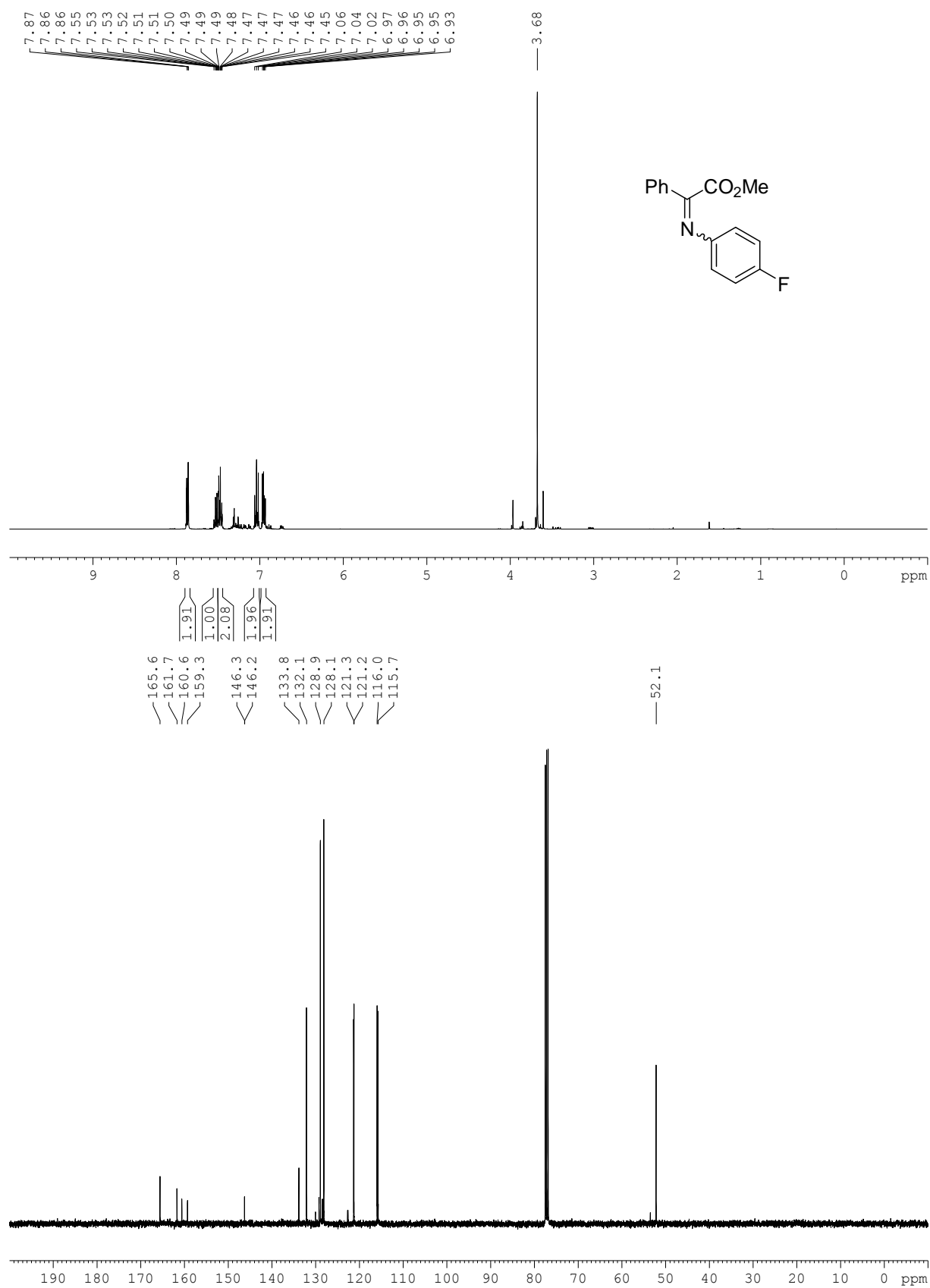
Compound from table 2, entry 8



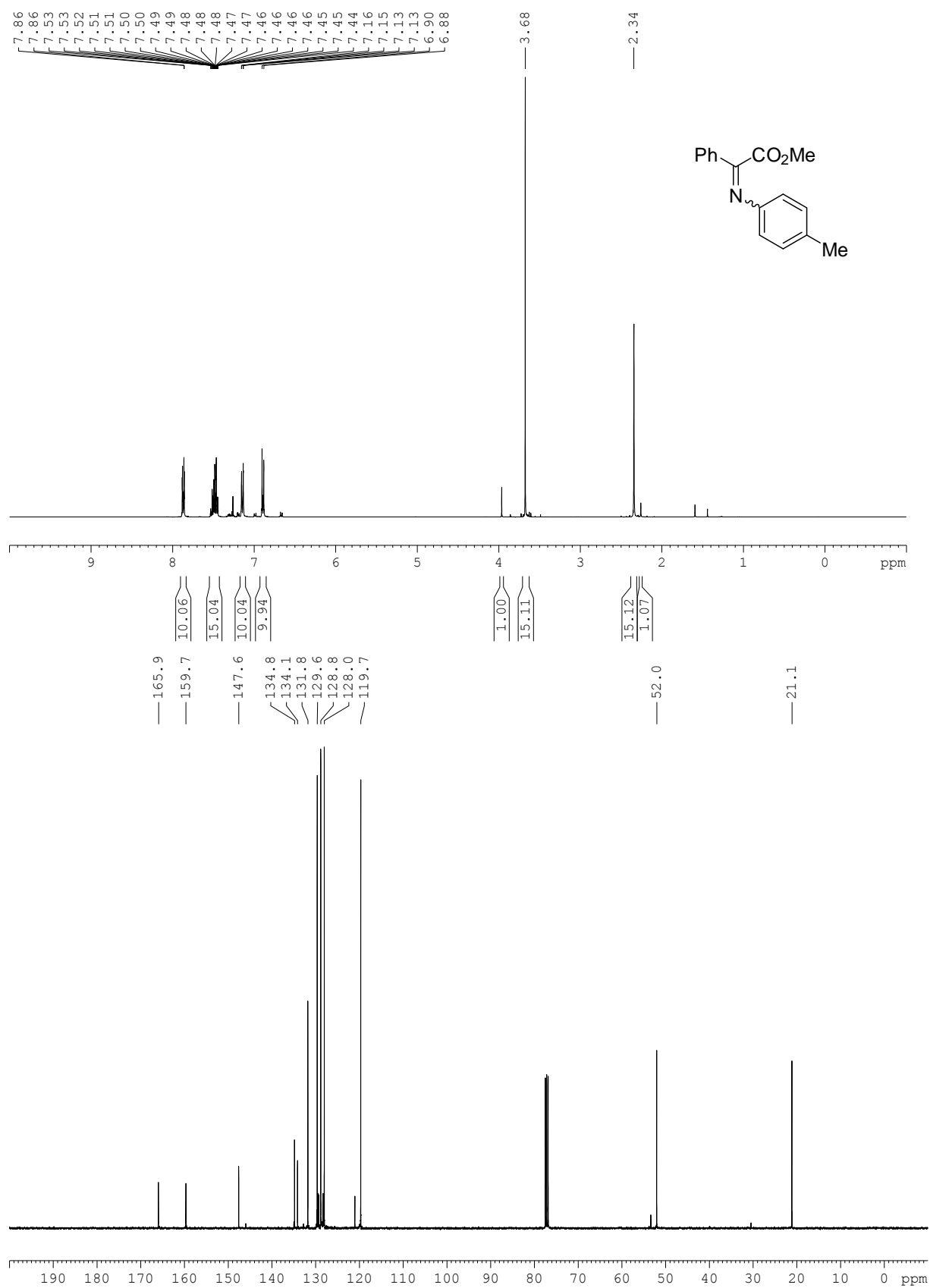
**Imine 17**



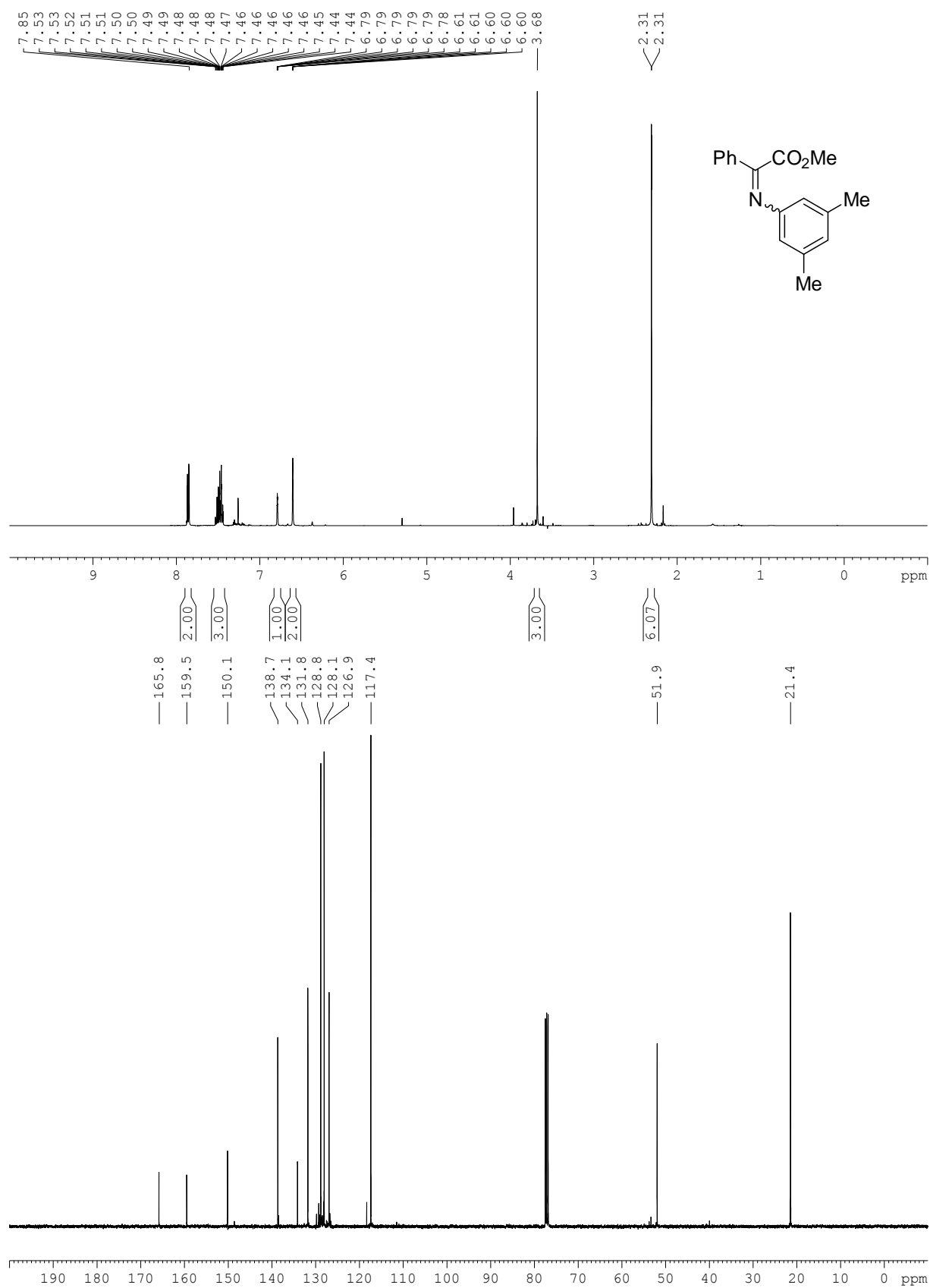
**Imine 21**



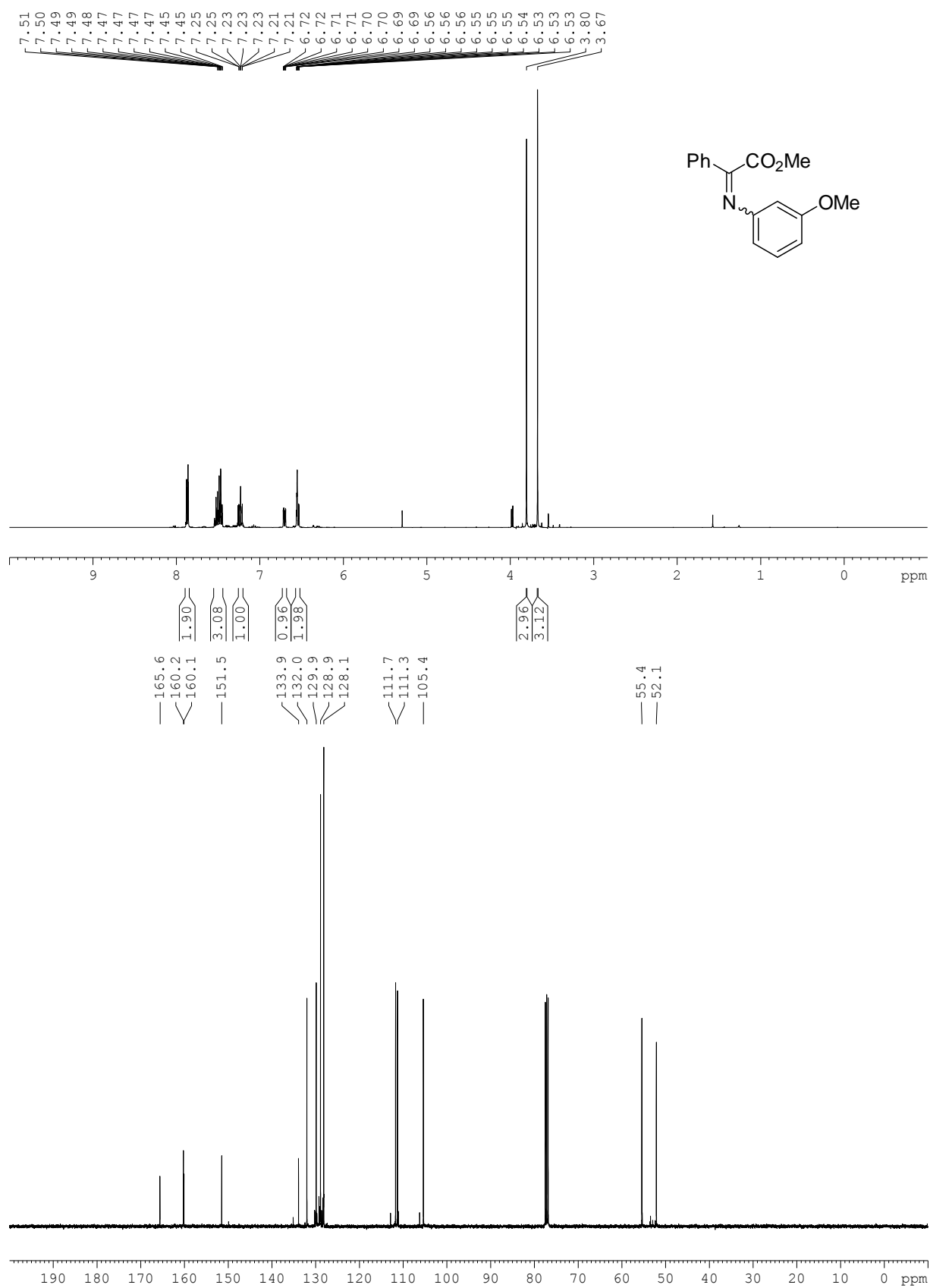
# Imine 18



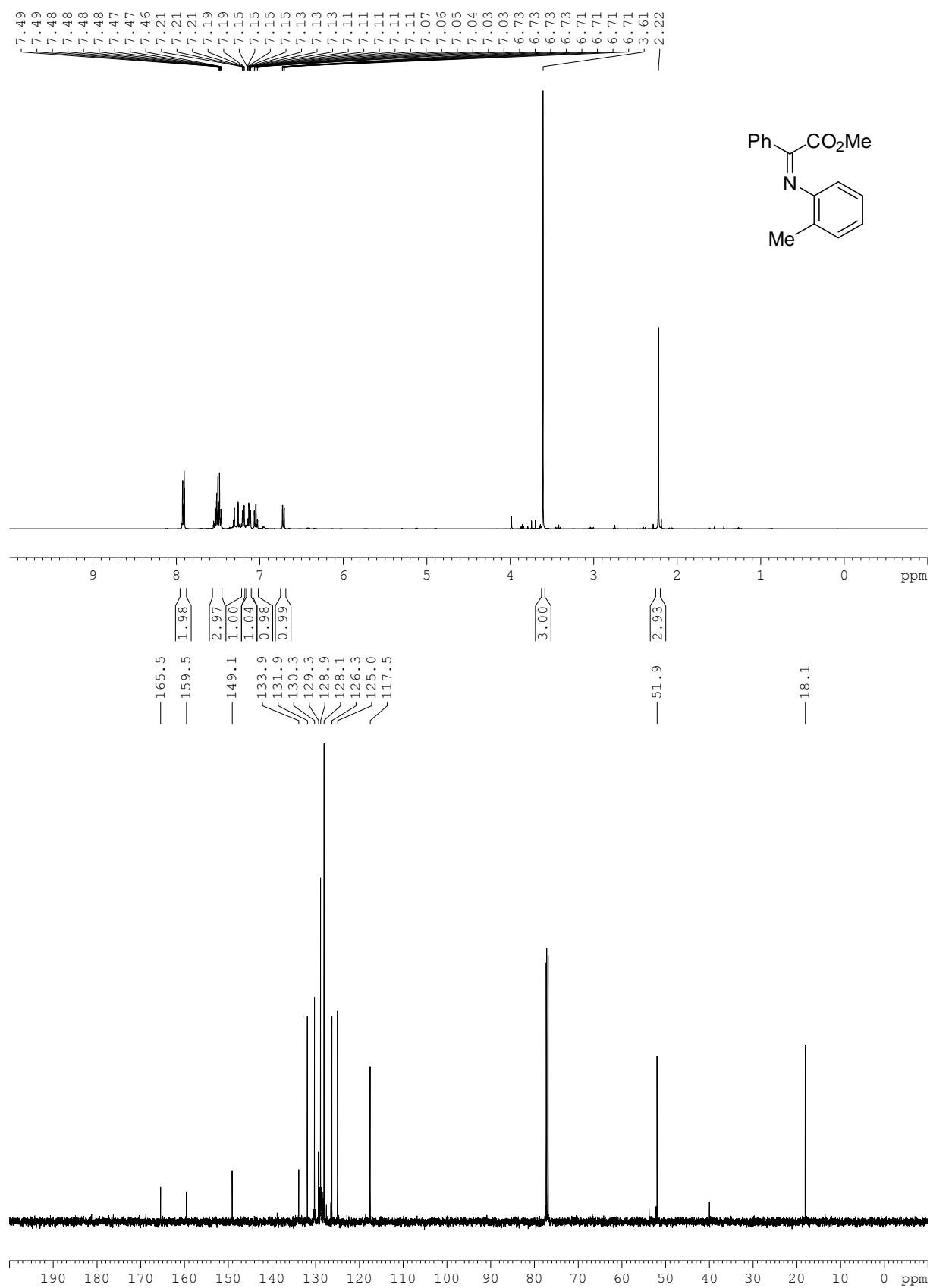
Imine 26



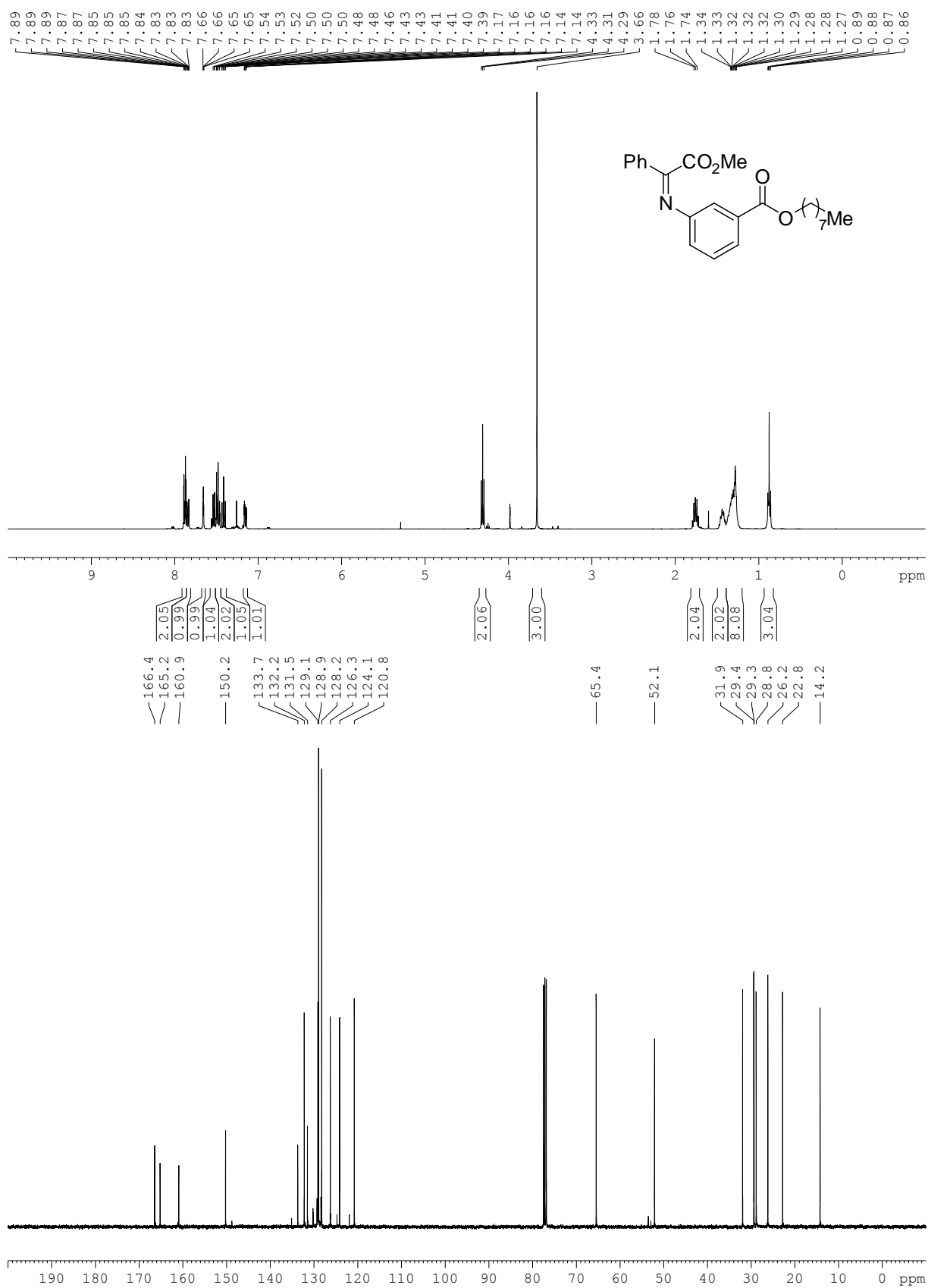
**Imine 24**



**Imine 23**

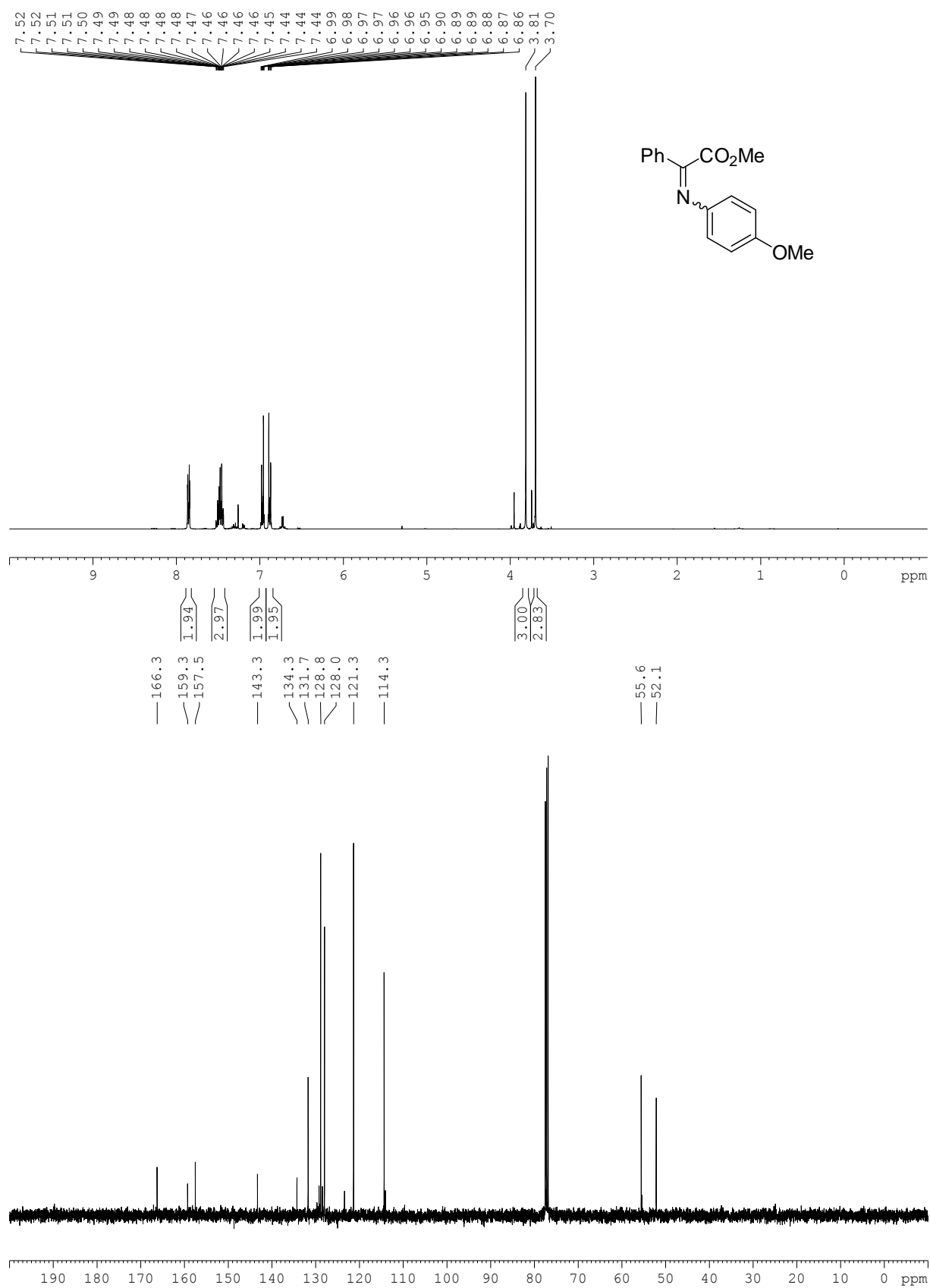


**Imine 25**

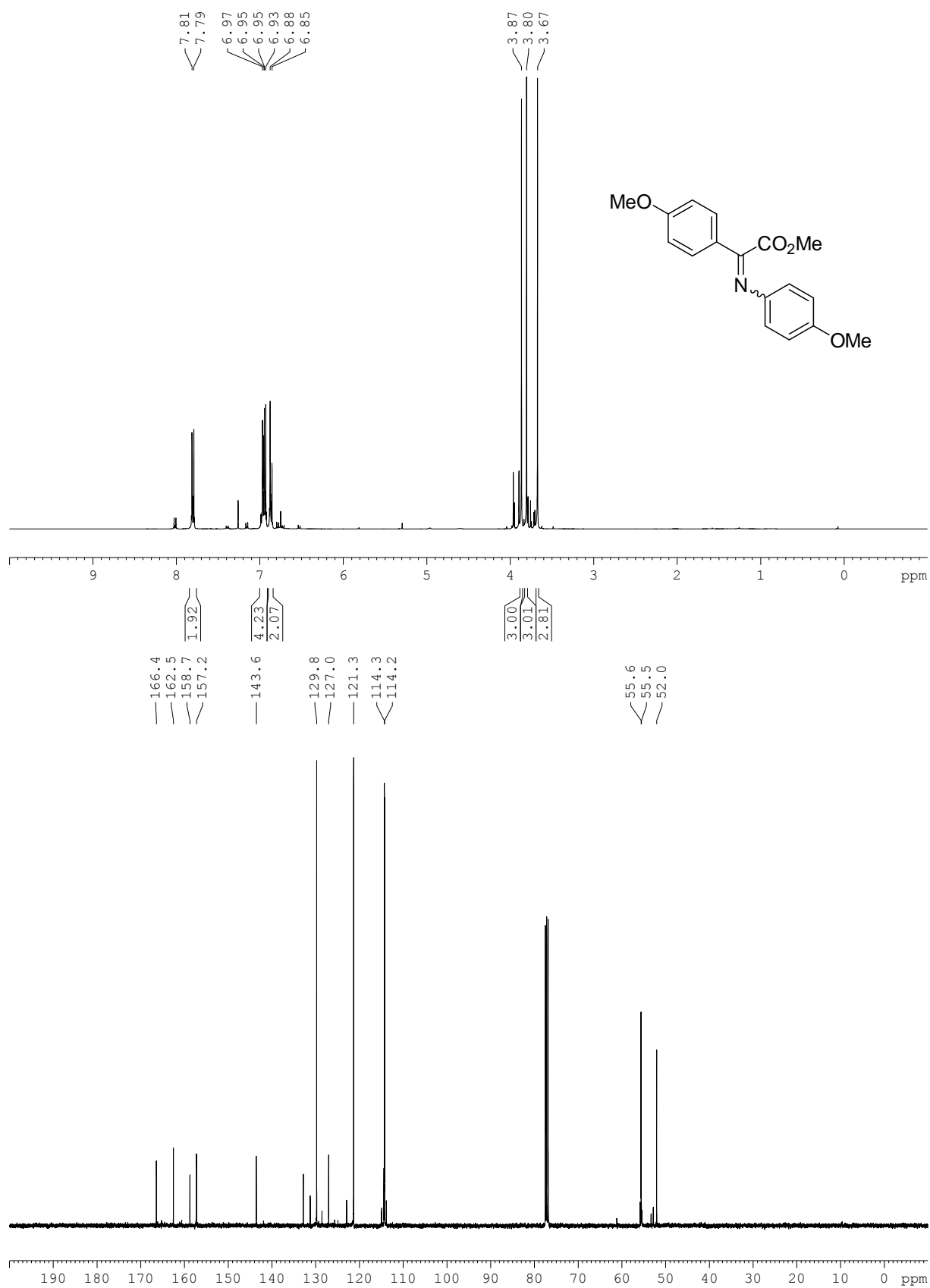




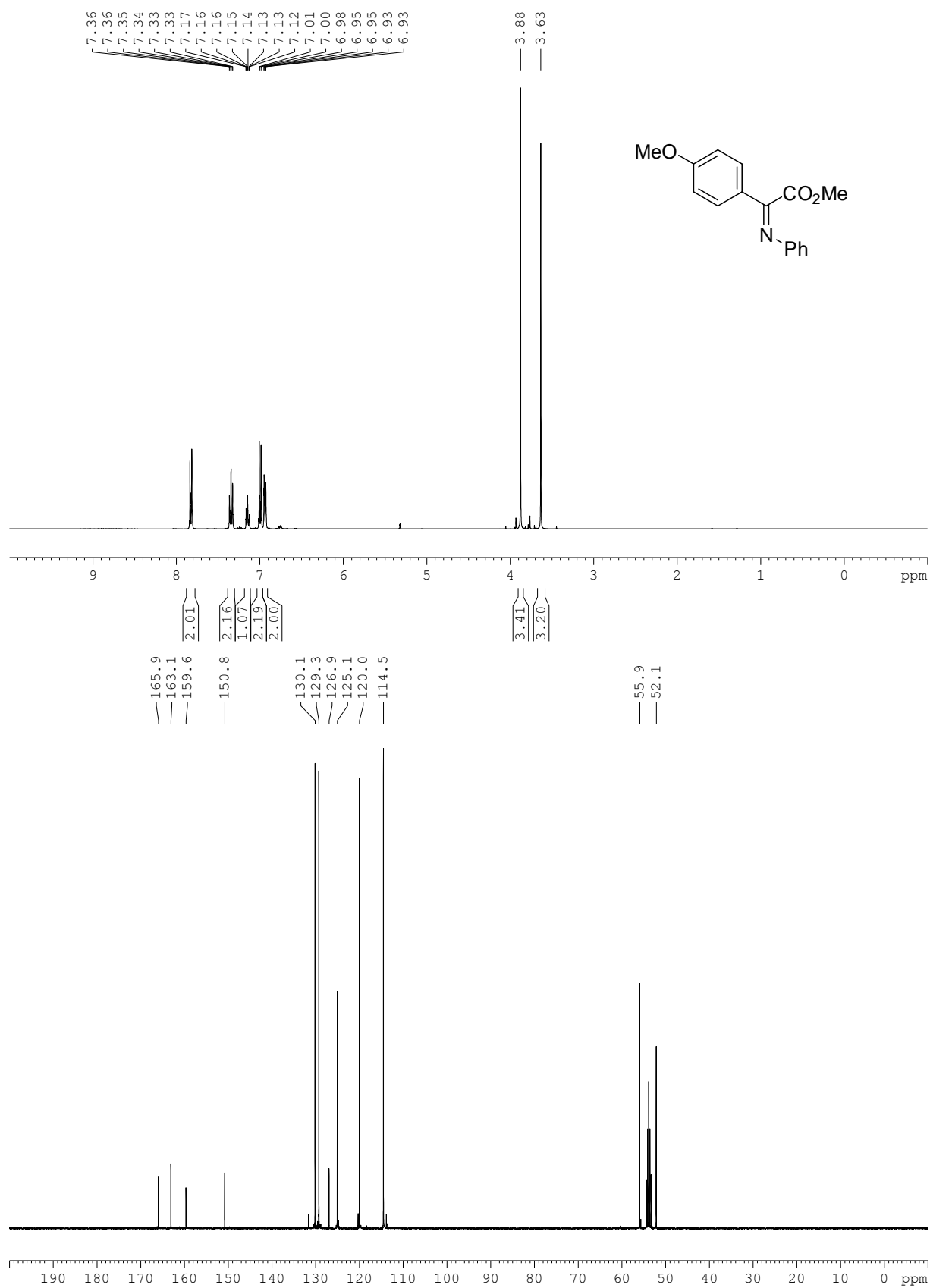
# Imine 19



# Imine 32



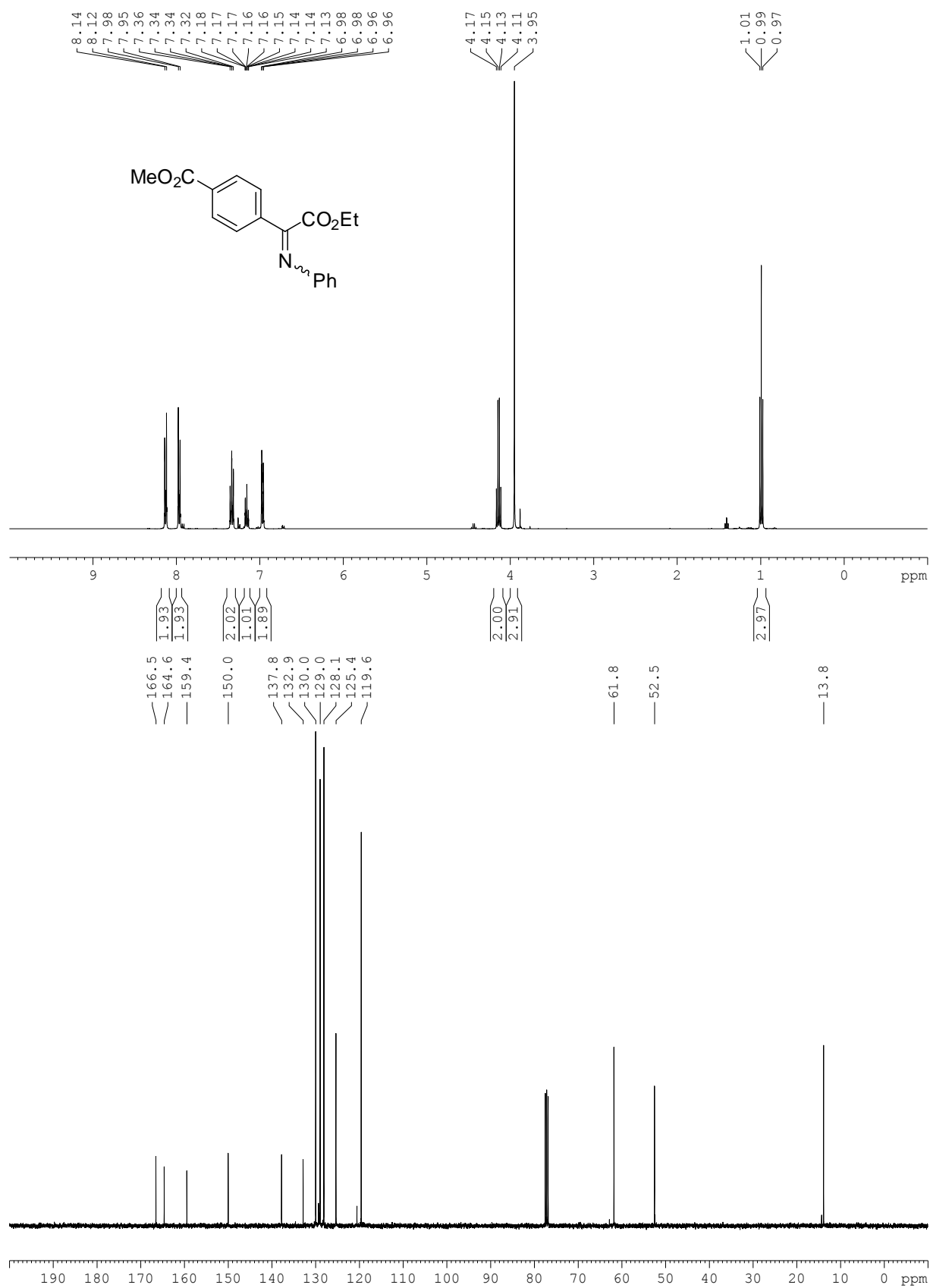
# Imine 31



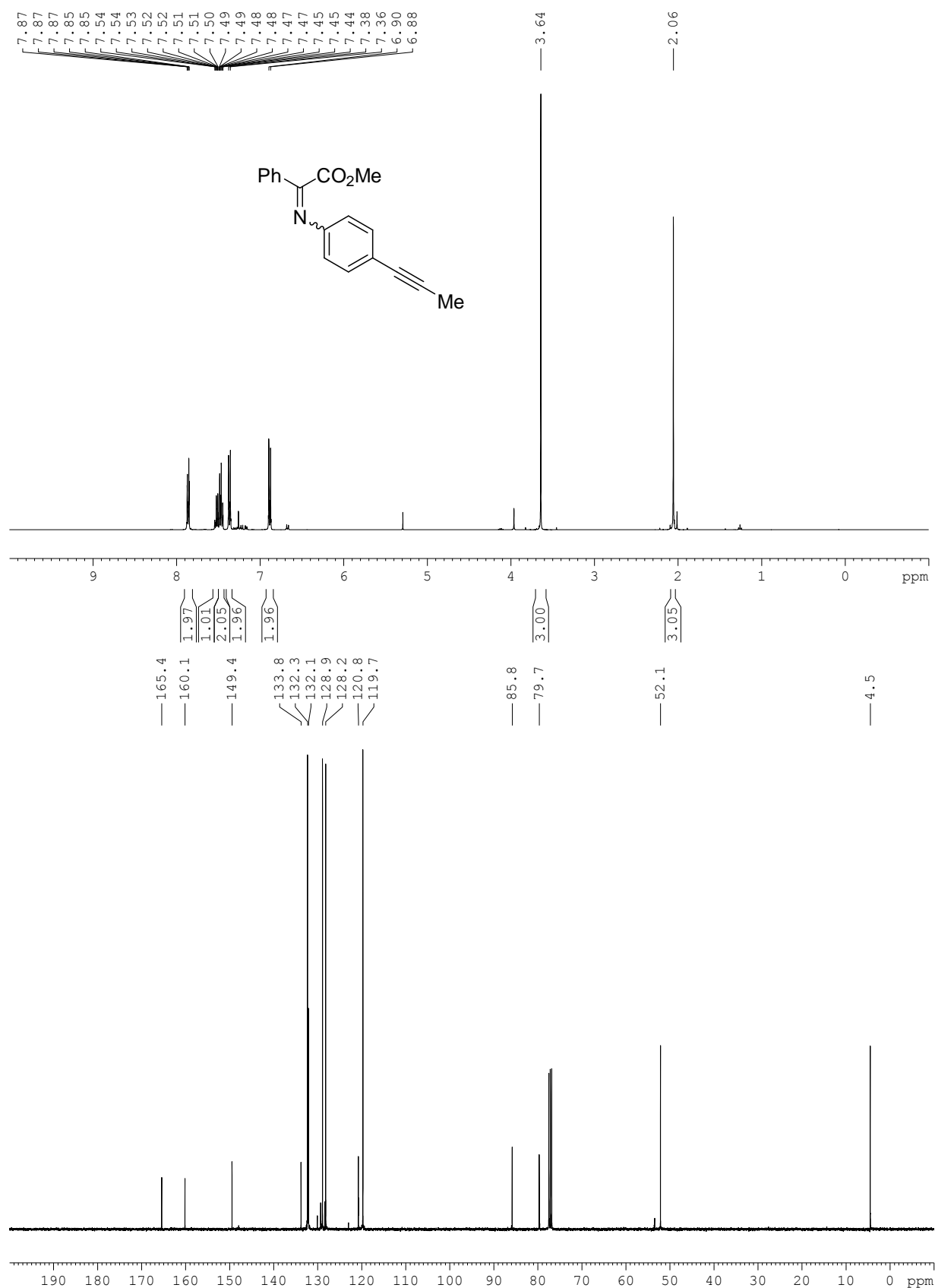
Imine 35



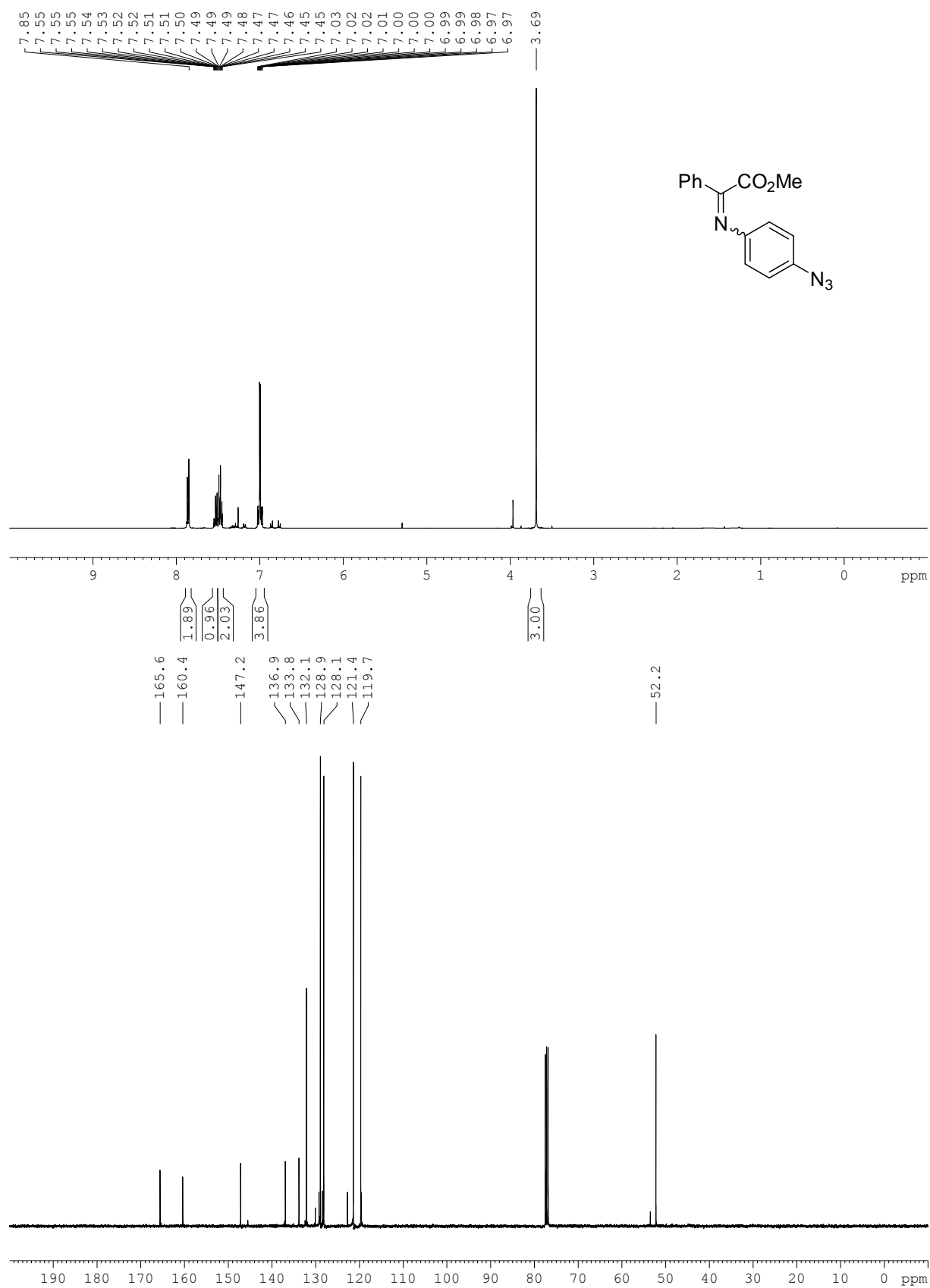
**Imine 34**



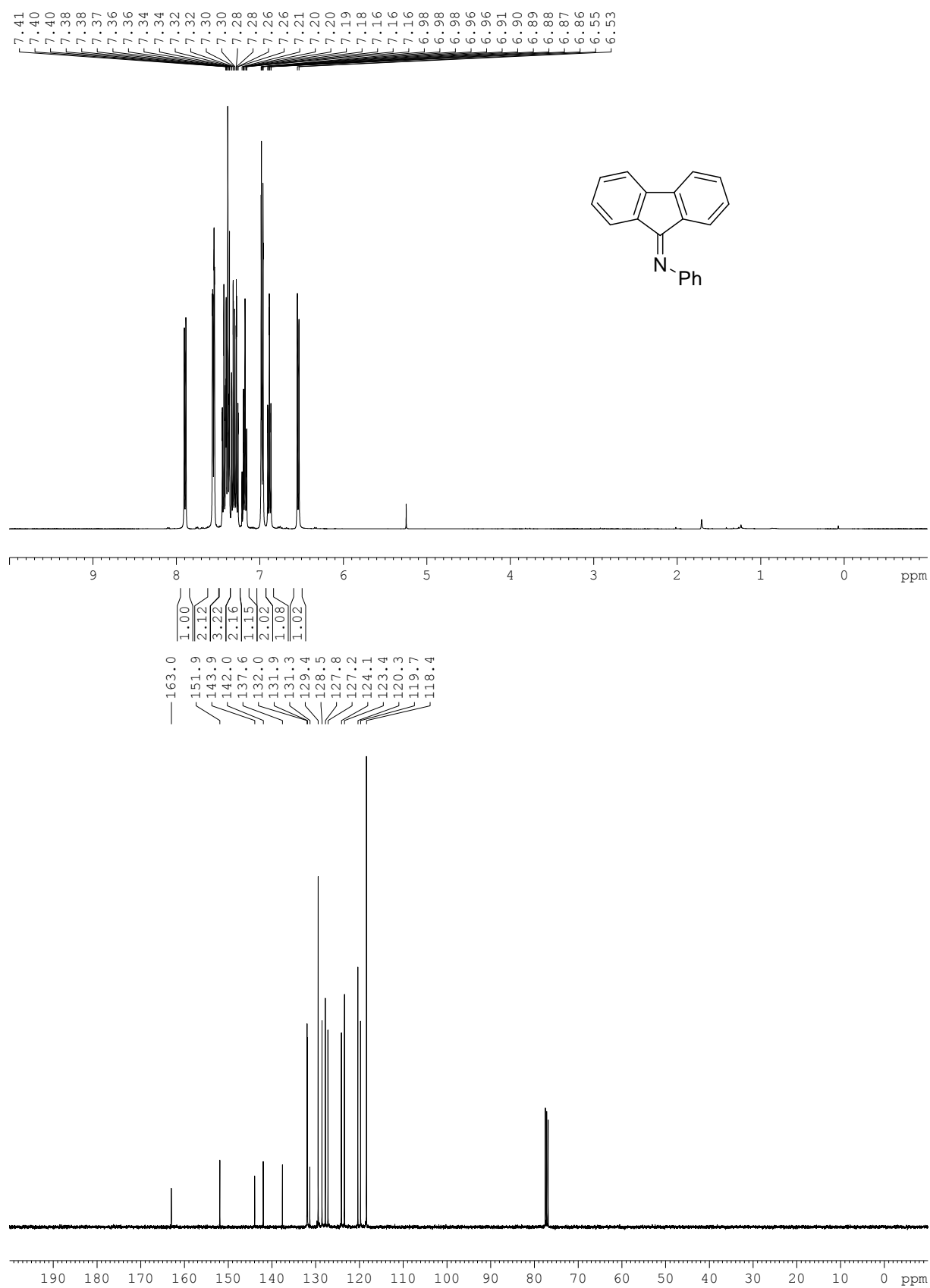
**Imine 29**



**Imine 30**



# Imine 37



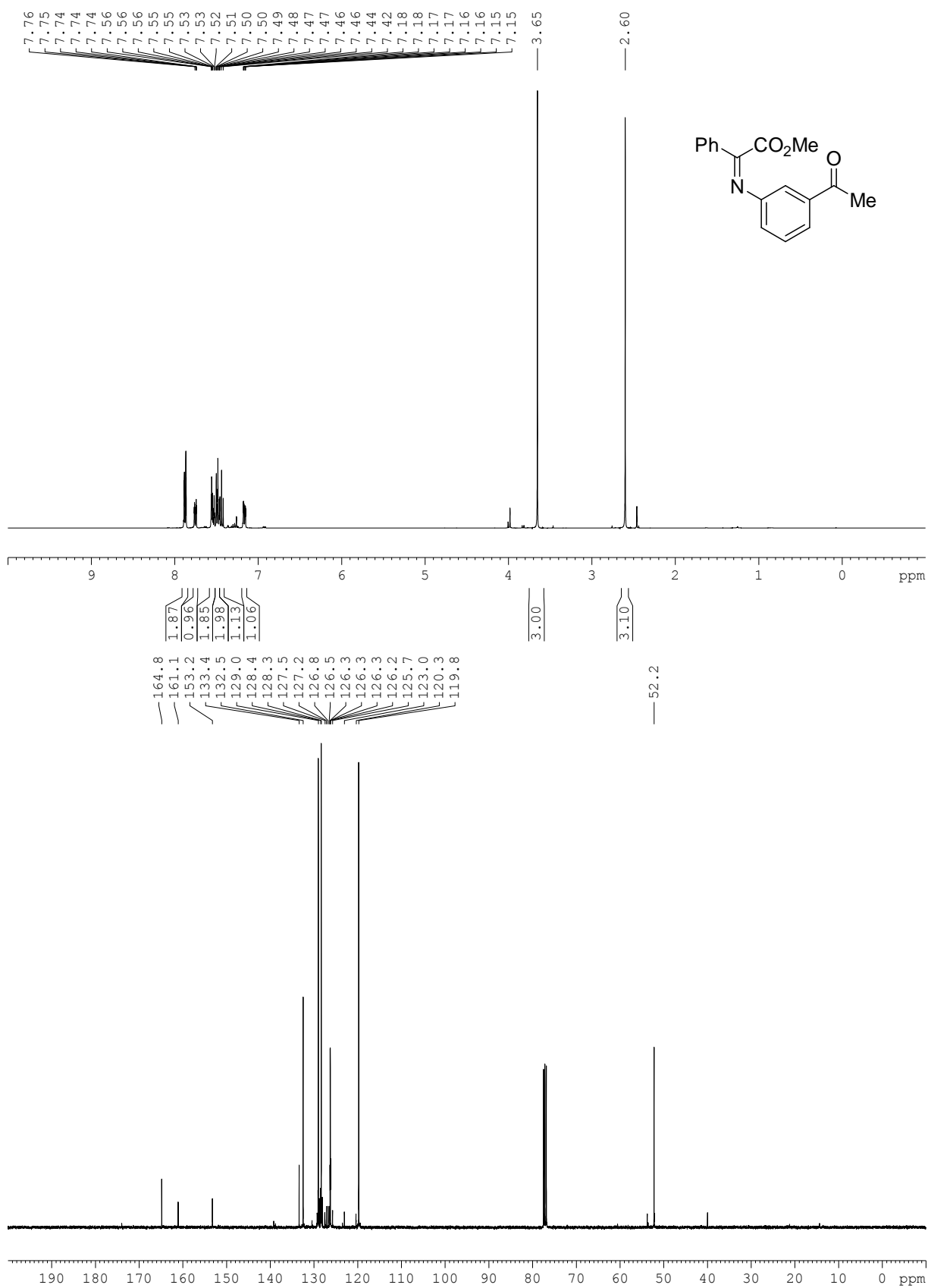




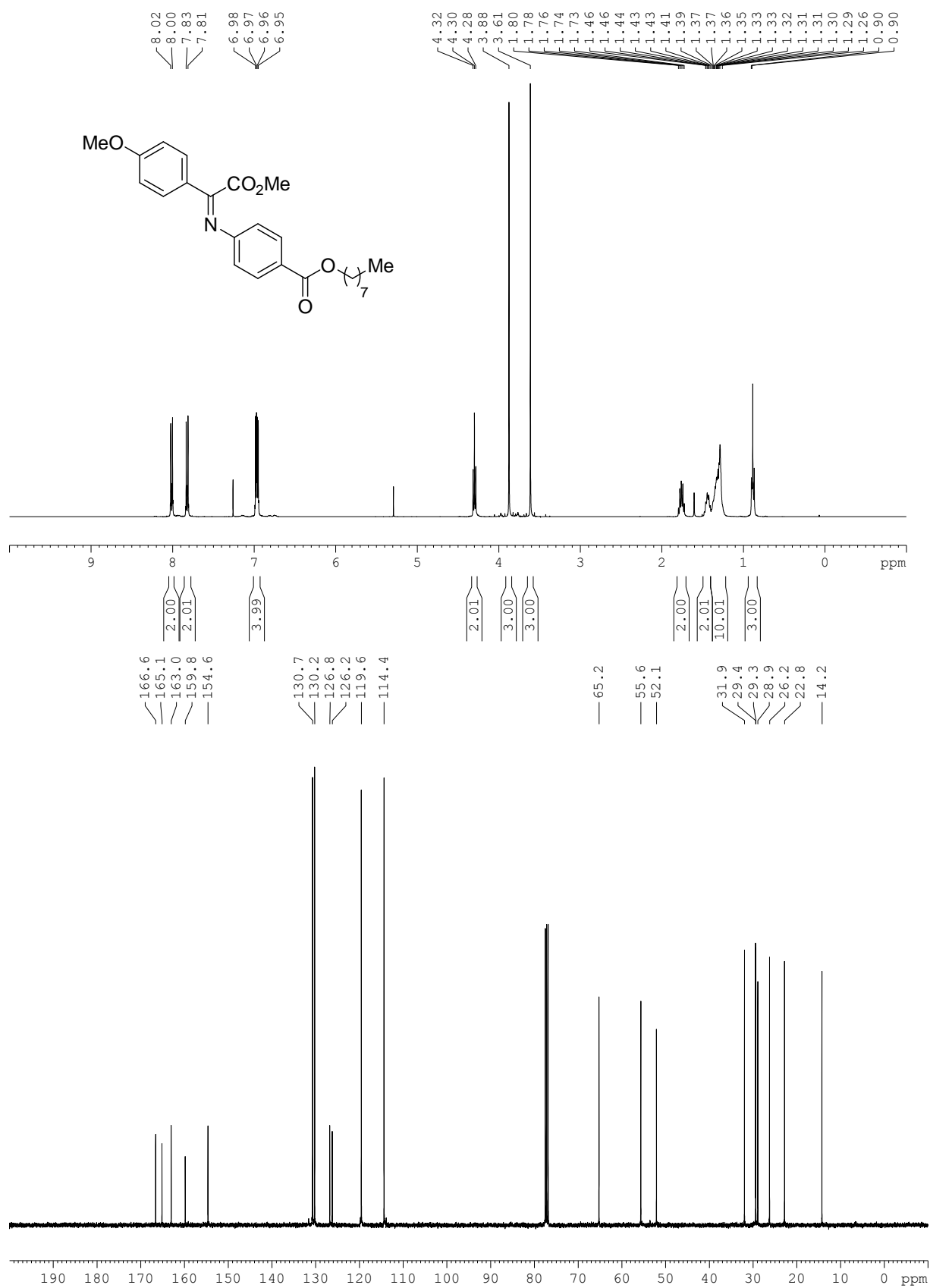
**Imine 22**



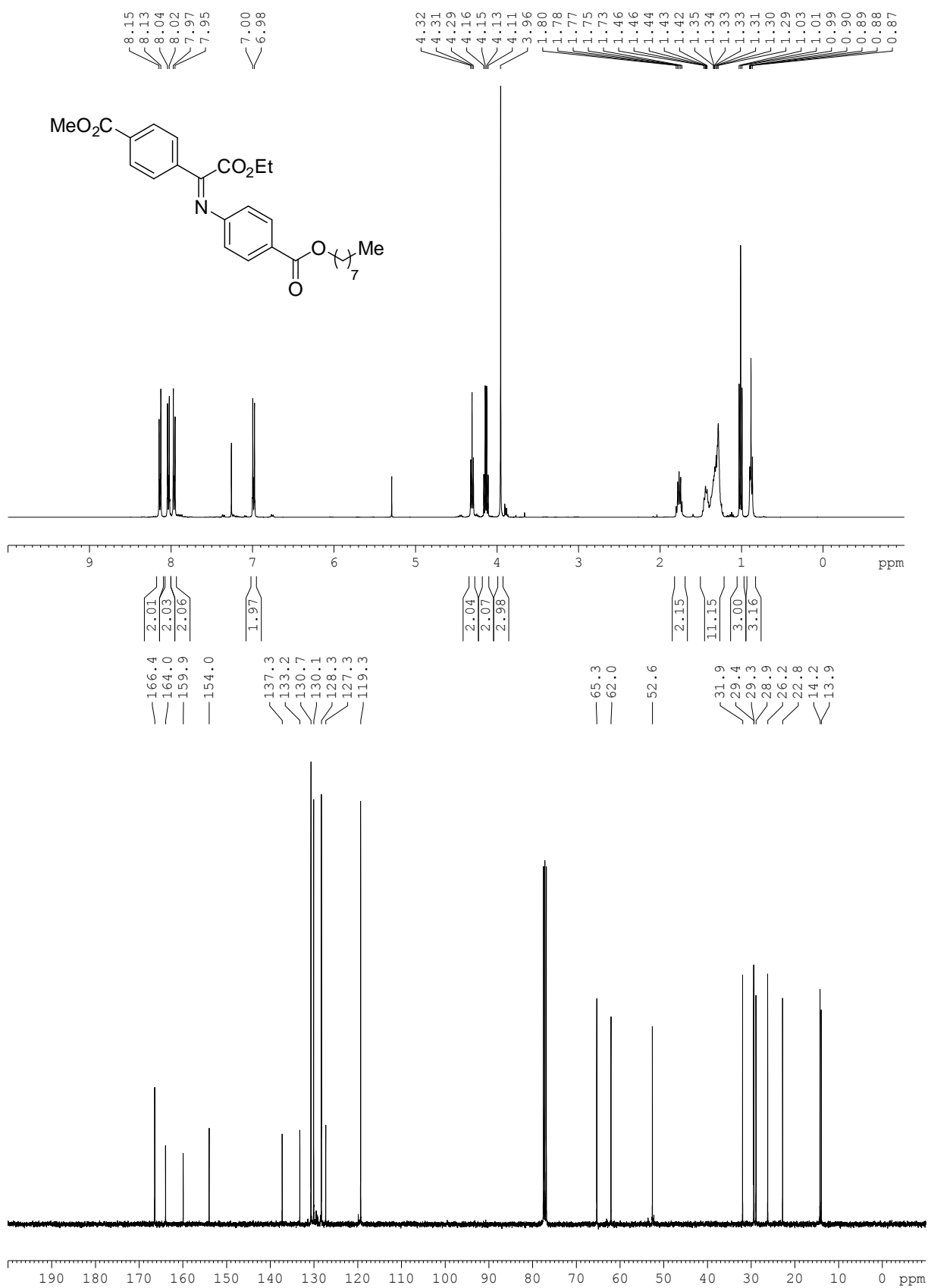
**Imine 28**



# Imine 33



**Imine 36**



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